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SECTION I

SUMMARY AND CONCLUSIONS

TOXIC POLLUTANTS

The following 34 inorganic chemical products were screened for the purpose of establishing wastewater effluent limitations guidelines for existing sources, standards of performance for new sources, and pretreatment standards for new and existing sources in this study:

1. Cadmium Pigments
2. Cadmium Chloride
3. Cadmium Nitrate
4. Cadmium Sulfate
5. Cobalt Chloride
6. Cobalt Nitrate
7. Cobalt Sulfate
8. Copper Carbonate
9. Copper Chloride
10. Copper Iodide
11. Copper Nitrate
12. Nickel Carbonate
13. Nickel Chloride
14. Nickel Fluoborate
15. Nickel Nitrate
16. Sodium Chlorate
17. Zinc Chloride
18. Calcium Hypochlorite
19. Bleaching Powders
20. Brine Chemicals
21. Potassium Bromide
22. Ammonium Thiosulfate
23. Chlorosulfonic Acid
24. Iron Oxide, Yellow
25. Iron Oxide, Black
26. Iron Oxide, Magnetic
27. Ochers
28. Siennas
29. Umbers
30. Iron Colors
31. Nitrous Oxide
32. Silica Gel
33. Silica Amorphous
34. Tin Compounds

The screening studies showed that only the plant process wastewaters from the first 17 subcategories contain significant quantities of toxic metals at treatable levels. (The Calcium Hypochlorite (Bleaching Powder) subcategory also generates treatable levels of toxic and nonconventional pollutants but that industry is intimately associated with the chlor-alkali industry and its pollutants are controlled by effluent limitations and standards for the chlor-alkali subcategory. See Section 19). Very few of the organic toxic pollutants were found in process waste streams and those that were identified were present at low level concentrations.

CONTROL AND TREATMENT TECHNOLOGY

A considerable amount of toxic pollutant removal is currently achieved in the industry by the existing control and treatment practices. Additional removal can be accomplished by the application of available and demonstrated technologies which would add to or modify existing treatment systems. Recovery of toxic metals for value or reuse in a process does not appear to be an attractive alternative in those industries where the product recovery practices now in effect do not already accomplish this.

The treatment of toxic metal-bearing waste streams results in the production of sludges or residues which are potentially hazardous and may require special means for handling and disposal under the Resource Conservation and Recovery Act (RCRA) regulations.

COSTS OF ADDITIONAL IN-PLANT TREATMENT

The estimated incremental costs of applying the candidate BAT treatment options represent a small proportion of the investment and operating and maintenance costs already committed to the existing BPT level treatment systems. These costs, however, vary widely from industry to industry and are highly dependent on site-specific factors.

SUBCATEGORIZATION

A review of the product/process basis for subcategorization of the inorganic chemical product subcategories designated for study revealed that certain modifications may be appropriate in the interest of developing effective regulations. The 17 subcategories were reduced to six on the basis of similar raw materials, processes, and treatment technologies. Two subdivisions were set up within three subcategories, cadmium pigments and salts, copper salts, and nickel salts. In the cadmium pigments and salts subcategory, two subdivisions are promulgated, (a) cadmium pigments and (b) cadmium salts. Separate mass limitations are promulgated because of significant differences in unit flows. In the copper salts subcategory, two subdivisions are promulgated, including (a) copper sulfate, copper chloride, copper iodide, and copper nitrate; and (b) copper carbonate. Separate mass limitations are promulgated because of significant differences in unit flows. The existing copper sulfate regulations are being replaced with a new copper salts subcategory which will include copper sulfate as well as the other copper salts. Likewise, in the nickel salts subcategory, two subdivisions are promulgated: (a) nickel sulfate, nickel chloride, nickel nitrate, and nickel fluoborate; and (b) nickel carbonate. Separate mass limitations are promulgated because of significant differences in unit flows. The existing nickel sulfate regulations are being replaced with a new nickel salts subcategory which will include nickel sulfate as well as the other nickel salts. In the zinc chloride subcategory, effluent limitations are based upon concentrations rather than mass loadings because the product(s) produced exert a significant influence on the unit flows, the marketplace will determine the product at any time, and because there is a very wide difference between unit flows at industry plants making different forms (liquid or solid) of the product. Plants producing solid zinc chloride also produce liquid zinc chloride using the same production equipment on different days.

BAT REVISIONS

In response to a petition from the Salt Institute, the study also included a reexamination of BAT for the sodium chloride (solution brine-mining process), sodium sulfite, and calcium chloride subcategories. Revisions of BAT are being promulgated for the sodium chloride and sodium sulfite subcategories. For sodium sulfite we also establish a new BCT equal to BPT, and a new NSPS and PSNS equal to the new BAT.

EXCLUDED SUBCATEGORIES

After thorough study and review, 104 subcategories are excluded primarly because the toxic and nonconventional pollutant discharges are insignificant or there are one or no discharging plants. In addition, as noted above, the calcium hypochlorite and bleaching powder subcategories (which are identical) are excluded because the calcium hypochlorite effluent is controlled by the technology on which chlor-alkali limitations are based. Development of regulations for the beryllium oxide subcategory is deferred for coverage under the nonferrous metals manufacturing point source category (Phase II), for which regulations will be promulgated later, because beryllium oxide is formed only during the manufacturing of beryllium metal.

SECTION II

RECOMMENDATIONS

On the basis of the toxic pollutant screening and verification results and the evaluation of applicable technologies for discharge control and treatment, it is recommended that effluent limitation guidelines, new source performance standards and pretreatment standards for new and existing sources be promulgated for the following six inorganic chemicals manufacturing subcategories:

Cadmium Pigments and Salts
Cobalt Salts
Copper Salts
Nickel Salts
Sodium Chlorate
Zinc Chloride

Table 2-1 summarizes the promulgated regulations for Best Practicable Control Technology Currently Available (BPT). Summaries of regulations for Best Available Technology (BAT), Pretreatment Standards for Existing Sources (PSES), New Source Performance Standards (NSPS), Pretreament Standards for New Sources (PSNS), and Best Conventional Pollutant Control Technology (BCT) are given in Tables 2-2, 2-3, 2-4, 2-5, and 2-6.

These tables also indicate that the cadmium pigments and salts, copper salts, and nickel salts subcategories are further subdivided into two segments.

New BAT and BCT effluent limitations and PSNS and NSPS are being promulgated for the sodium sulfite subcategory. These limitations are summarized in Tables 2-2, 2-4, 2-5, and 2-6. The Agency is revoking the existing BAT effluent limitations for the sodium chloride (solution brine-mining process) and replacing it with a BCT effluent limitation.

The Agency is excluding 104 subcategories and also excluding two subcategories because discharges are controlled by existing regulations: calcium hypochlorite and bleaching powder. Beryllium oxide is deferred to future regulations in the nonferrous metals category (Phase II). The Agency is also excluding 23 subcategories deferred from the inorganic chemicals Phase I PSES regulation development from further national PSES regulation. One of the 23 subcategories, hydrogen, is already covered under existing limitations for the petroleum refining category.

TABLE 2-1

SUMMARY OF REGULATIONS - BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPT)

Subcategory	Parameter	Effluent Limitations Max 30-day Avg	 24-hr Max
		kg/kkg (or lb/1000 lb) of Product	
Cadmium Pigments	TSS	1.57	2.59
	Cadmium (T)	0.026	0.078
	Selenium (T)	0.037	0.11
	Zinc (T)	0.0092	0.017
	pH	(1)	(1)
Cadmium Salts	TSS	0.001	0.0016
	Cadmium (T)	0.0000162	0.0000487
	Selenium (T)	0.000023	0.000070
	Zinc (T)	0.0000058	0.0000104
	pH	(1)	(1)
Cobalt Salts	TSS	0.0014	0.0023
	Cobalt (T)	0.00012	0.00030
	Copper (T)	0.000083	0.00027
	Nickel (T)	0.000083	0.00027
	pH	(1)	(1)
Copper Salts ($CuSO_4$, $CuCl_2$, CuI, $Cu(NO_3)_2$)	TSS	0.023	0.069
	Copper (T)	0.0010	0.0030
	Nickel (T)	0.0020	0.0060
	Selenium (T)	0.00050	0.0015
	pH	(1)	(1)
Copper Salts ($CuCO_3$)	TSS	1.4	4.2
	Copper (T)	0.064	0.19
	Nickel (T)	0.12	0.37
	Selenium (T)	0.031	0.093
	pH	(1)	(1)
Nickel Salts ($NiSO_4$, $NiCl_2$, $Ni(NO_3)_2$, $Ni(BF_4)_2$)	TSS	0.032	0.096
	Nickel (T)	0.002	0.006
	pH	(1)	(1)
Nickel Salts ($NiCO_3$)	TSS	5.6	17
	Nickel (T)	0.36	1.1
	pH	(1)	(1)

(1) Within the range 6.0 to 9.0

TABLE 2-1 (Continued)

SUMMARY OF REGULATIONS - BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPT)

Subcategory	Parameter	Effluent Limitations	
		Max 30-day Avg	24-hr Max
		kg/kkg (or lb/1000 lb) of Product	
Sodium Chlorate	TSS	0.068	0.12
	Antimony(T)	0.0043	0.0086
	Chromium (T)	0.0014	0.0027
	Chlorine (Total Residual)	0.0024	0.0041
	pH	(1)	(1)
		mg/l(ppm)	
Zinc Chloride	TSS	25	43
	Arsenic (T)	1.0	3.0
	Zinc (T)	3.8	11.4
	Lead (T)	0.6	1.8
	pH	(2)	(2)

(1) Within the range 6.0 to 9.0
(2) Within the range 6.0 to 10.0

TABLE 2-2

SUMMARY OF REGULATIONS - BEST AVAILABLE TECHNOLOGY (BAT)

Subcategory	Parameter	Effluent Limitations	
		Max 30-day Avg	24-hr Max
		kg/kkg (or lb/1000 lb) of Product	
Cadmium Pigments	Cadmium (T)	same as BPT	same as BPT
	Selenium (T)	same as BPT	same as BPT
	Zinc (T)	same as BPT	same as BPT
Cadmium Salts	Cadmium (T)	same as BPT	same as BPT
	Selenium (T)	same as BPT	same as BPT
	Zinc (T)	same as BPT	same as BPT
Cobalt Salts	Cobalt (T)	same as BPT	same as BPT
	Copper (T)	same as BPT	same as BPT
	Nickel (T)	same as BPT	same as BPT
Copper Salts ($CuSO_4$, $CuCl_2$, CuI, $Cu(NO_3)_2$)	Copper (T)	same as BPT	same as BPT
	Nickel (T)	same as BPT	same as BPT
	Selenium (T)	same as BPT	same as BPT
Copper Salts ($CuCO_3$)	Copper (T)	same as BPT	same as BPT
	Nickel (T)	same as BPT	same as BPT
	Selenium (T)	same as BPT	same as BPT
Nickel Salts ($NiSO_4$, $NiCl_2$, $Ni(NO_3)_2$, $Ni(BF_4)_2$)	Copper (T)	0.00024	0.00074
	Nickel (T)	0.00024	0.00074
Nickel Salts ($NiCO_3$)	Copper (T)	0.042	0.13
	Nickel (T)	0.042	0.13
Sodium Chlorate	Antimony	0.0022	0.0043
	Chromium(T)	0.00086	0.0017
	Chlorine (Total Residual)	0.0024	0.0041
		mg/l(ppm)	
Zinc Chloride	Arsenic (T)	1.0	3.0
	Zinc (T)	0.76	2.3
	Lead (T)	0.048	0.18

TABLE 2-2 (Continued)

SUMMARY OF REGULATIONS - BEST AVAILABLE TECHNOLOGY (BAT)

Subcategory	Parameter	Effluent Limitations	
		Max 30-day Avg	24-hr Max
		kg/kkg (or lb/1000 lb) of Product	
Sodium Chloride (Solution Brine Mining Process)	-	Reserved	
Sodium Sulfite	Chromium(T)	0.00063	0.0020
	Zinc (T)	0.0015	0.0051
	COD	1.7	3.4

TABLE 2-3

SUMMARY OF REGULATIONS - PRETREATMENT STANDARDS FOR EXISTING SOURCES (PSES)

Subcategory	Parameter	Effluent Limitations			
		Max 30-day Avg		24-hr Max	
		mg/l	kg/kkg	mg/l	kg/kkg
Cadmium Pigments	Cadmium (T)	0.28	0.026	0.84	0.078
	Selenium (T)	0.40	0.037	1.1	0.11
	Zinc (T)	0.10	0.0092	0.18	0.017
Cadmium Salts	Cadmium (T)	0.28	0.0000162	0.84	0.0000487
	Selenium (T)	0.40	0.000023	1.1	0.000070
	Zinc (T)	0.10	0.0000058	0.18	0.0000104
Cobalt Salts	Cobalt (T)	1.4	0.00012	3.6	0.00030
	Copper (T)	1.0	0.000083	3.3	0.00027
	Nickel (T)	1.0	0.000083	3.3	0.00027
Copper Salts ($CuSO_4$, $CuCl_2$, CuI, $Cu(NO_3)_2$)	Copper (T)	1.1	0.0010	3.2	0.0030
	Nickel (T)	2.1	0.0020	6.4	0.0060
	Selenium (T)	0.53	0.00050	1.6	0.0015
Copper Salts ($CuCO_3$)	Copper (T)	1.1	0.064	3.2	0.19
	Nickel (T)	2.1	0.12	6.4	0.37
	Selenium (T)	0.53	0.031	1.6	0.093
Nickel Salts ($NiSO_4$, $NiCl_2$, $Ni(NO_3)_2$, $Ni(BF_4)_2$)	Copper(T)	0.36	0.00024	1.1	0.00074
	Nickel(T)	0.36	0.00024	1.1	0.00074
Nickel Salts ($NiCO_3$)	Copper(T)	0.36	0.042	1.1	0.13
	Nickel(T)	0.36	0.042	1.1	0.13
Sodium Chlorate	-	Reserved			
Zinc Chloride	Arsenic (T)	1.0		3.0	
	Zinc (T)	0.76		2.3	
	Lead (T)	0.048		0.18	

TABLE 2-4

SUMMARY OF REGULATIONS - NEW SOURCE PERFORMANCE STANDARDS (NSPS)

Subcategory	Parameter	Effluent Limitations	
		Max 30-day Avg	24-hr Max
		kg/kkg (or lb/1000 lb) of Product	
Cadmium Pigments	TSS	1.57	2.59
	Cadmium (T)	0.026	0.078
	Selenium (T)	0.037	0.11
	Zinc (T)	0.0092	0.017
	pH	(1)	(1)
Cadmium Salts	TSS	0.001	0.0016
	Cadmium (T)	0.0000162	0.0000487
	Selenium (T)	0.000023	0.000070
	Zinc (T)	0.0000058	0.0000104
	pH	(1)	(1)
Cobalt Salts	TSS	0.0014	0.0023
	Cobalt (T)	0.00012	0.00030
	Copper (T)	0.000083	0.00027
	Nickel (T)	0.000083	0.00027
	pH	(1)	(1)
Copper Salts (CuSO$_4$, CuCl$_2$, CuI, Cu(NO$_3$)$_2$)	TSS	0.023	0.069
	Copper (T)	0.0010	0.0030
	Nickel (T)	0.0020	0.0060
	Selenium (T)	0.00050	0.0015
	pH	(1)	(1)
Copper Salts (CuCO$_3$)	TSS	1.4	4.2
	Copper (T)	0.064	0.19
	Nickel (T)	0.12	0.37
	Selenium (T)	0.031	0.093
	pH	(1)	(1)
Nickel Salts (NiSO$_4$, NiCl$_2$, Ni(NO$_3$)$_2$, Ni(BF$_4$)$_2$)	TSS	0.032	0.096
	Copper(T)	0.00024	0.00074
	Nickel (T)	0.00024	0.00074
	pH	(1)	(1)
Nickel Salts (NiCO$_3$)	TSS	5.6	17
	Copper(T)	0.042	0.13
	Nickel (T)	0.042	0.13
	pH	(1)	(1)

(1) Within the range 6.0 to 9.0

TABLE 2-4 (Continued)

SUMMARY OF REGULATIONS - NEW SOURCE PERFORMANCE STANDARDS (NSPS)

Subcategory	Parameter	Effluent Limitations Max 30-day Avg	 24-hr Max
		kg/kkg (or lb/1000 lb) of Product	
Sodium Chlorate	TSS	0.046	0.076
	Antimony(T)	0.0022	0.0043
	Chromium (T)	0.00086	0.0017
	Chlorine (Total Residual)	0.0024	0.0041
	pH	(1)	(1)
		mg/l(ppm)	
Zinc Chloride	TSS	17	28
	Arsenic (T)	1.0	3.0
	Zinc (T)	0.76	2.3
	Lead (T)	0.048	0.18
	pH	(2)	(2)
		kg/kkg (or lb/1000 lb) of product	
Sodium Sulfite	TSS	0.016	0.032
	Chromium(T)	0.00063	0.0020
	Zinc(T)	0.0015	0.0051
	COD	1.7	3.4
	pH	(1)	(1)

(1) Within the range 6.0 to 9.0
(2) Within the range 6.0 to 10.0

TABLE 2-5

SUMMARY OF REGULATIONS - PRETREATMENT STANDARDS FOR NEW SOURCES (PSNS)

Subcategory	Parameter	Effluent Limitations			
		Max 30-day Avg		24-hr Max	
		mg/l	kg/kkg	mg/l	kg/kkg
Cadmium Pigments	Cadmium (T)	same as PSES		same as PSES	
	Selenium (T)	same as PSES		same as PSES	
	Zinc (T)	same as PSES		same as PSES	
Cadmium Salts	Cadmium (T)	same as PSES		same as PSES	
	Selenium (T)	same as PSES		same as PSES	
	Zinc (T)	same as PSES		same as PSES	
Cobalt Salts	Cobalt (T)	same as PSES		same as PSES	
	Copper (T)	same as PSES		same as PSES	
	Nickel (T)	same as PSES		same as PSES	
Copper Salts ($CuSO_4$, $CuCl_2$, CuI, $Cu(NO_3)_2$)	Copper (T)	same as PSES		same as PSES	
	Nickel (T)	same as PSES		same as PSES	
	Selenium (T)	same as PSES		same as PSES	
Copper Salts ($CuCO_3$)	Copper (T)	same as PSES		same as PSES	
	Nickel (T)	same as PSES		same as PSES	
	Selenium (T)	same as PSES		same as PSES	
Nickel Salts ($NiSO_4$, $NiCl_2$, $Ni(NO_3)_2$, $Ni(BF_4)_2$)	Copper (T)	same as PSES		same as PSES	
	Nickel (T)	same as PSES		same as PSES	
Nickel Salts ($NiCO_3$)	Copper (T)	same as PSES		same as PSES	
	Nickel (T)	same as PSES		same as PSES	
Sodium Chlorate	Chromium(T)	0.32	0.00086	0.64	0.0017
	Antimony(T)	0.8	0.0022	1.6	0.0043

TABLE 2-5

SUMMARY OF REGULATIONS - PRETREATMENT STANDARDS FOR NEW SOURCES (PSNS)

Subcategory	Parameter	Effluent Limitations			
		Max 30-day Avg		24-hr Max	
		mg/l	kg/kkg	mg/l	kg/kkg
Zinc Chloride	Arsenic (T)	same as PSES		same as PSES	
	Zinc (T)	same as PSES		same as PSES	
	Lead (T)	same as PSES		same as PSES	
Sodium Sulfite	Chromium(T)	0.42	0.00063	1.3	0.0020
	Zinc(T)	1.2	0.0015	3.4	0.0051
	COD	630	1.7	1260	3.4

TABLE 2-6

SUMMARY OF REGULATIONS - BEST CONVENTIONAL POLLUTANT CONTROL TECHNOLOGY (BCT)

Subcategory	Parameter	Effluent Limitations	
		Max 30-day Avg	24-hr Max
		kg/kkg (or lb/1000 lb) of Product	
Cadmium Pigments	TSS pH	same as BPT (1)	same as BPT (1)
Cadmium Salts	TSS pH	same as BPT (1)	same as BPT (1)
Cabalt Salts	TSS pH	same as BPT (1)	same as BPT (1)
Copper Salts ($CuSO_4$, $CuCl_2$, CuI, $Cu(NO_3)_2$)	TSS pH	same as BPT (1)	same as BPT (1)
Copper Salts ($CuCO_3$)	TSS pH	same as BPT (1)	same as BPT (1)
Nickel Salts ($NiSO_4$, $NiCl_2$, $Ni(NO_3)_2$, $Ni(BF_4)_2$)	TSS pH	same as BPT (1)	same as BPT (1)
Nickel Salts ($NiCO_3$)	TSS pH	same as BPT (1)	same as BPT (1)
Sodium Chlorate	TSS pH	same as BPT (1)	same as BPT (1)
Zinc Chloride	TSS pH	same as BPT (2)	same as BPT (2)
Sodium Chloride (Solution Brine-Mining Process)	TSS pH	reserved	reserved
Sodium Sulfite	TSS pH	same as BPT (1)	same as BPT (1)

(1) Within the range 6.0 to 9.0

(2) Within the range 6.0 to 10.0

The Agency is proposing PSNS of no discharge for 12 of those 23 subcategories; the other 11 of those 23 subcategories are regulated by currently effective PSNS.

SECTION 3

INTRODUCTION

AUTHORITY

The Federal Water Pollution Control Act Amendments

The Federal Water Pollution Control Act (the Act) Amendments of 1972, 33 USC 1251 et seq., stated the national goal of attaining by July 1, 1983, a water quality which provides for the protection and propagation of fish and shellfish, for recreation in or on the nation's waters, and the goal of eliminating the discharge of pollutants into navigable waters by 1985.

Purpose and Authority

The Federal Water Pollution Control Act Amendments of 1972 established a comprehensive program to "restore and maintain the chemical, physical, and biological integrity of the Nation's waters," Section 101(a). By July 1, 1977, existing industrial dischargers were required to achieve "effluent limitations requiring the application of the best practicable control technology currently available" ("BPT"), Section 301(b)(1)(A); and by July 1, 1983, these dischargers were required to achieve "effluent limitations requiring the application of the best available technology economically achievable ("BAT")...which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants" Section 301(b)(2)(A). New industrial direct dischargers were required to comply with Section 306 new source performance standards ("NSPS"), based on best available demonstrated technology; and new and existing dischargers to publicly owned treatment works ("POTW") were subject to pretreatment standards under Sections 307(b) and (c) of the Act. While the requirements for direct dischargers were to be incorporated into National Pollutant Discharge Elimination System (NPDES) permits issued under Section 402 of the Act, pretreatment standards were made enforceable directly against dischargers to POTW (indirect dischargers).

Although Section 402(a)(1) of the 1972 Act authorized the setting of requirements for direct dischargers on a case-by-case basis, Congress intended that, for the most part, control requirements would be based on regulations promulgated by the Administrator of EPA. Section 304(b) of the Act required the Administrator to promulgate regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of BPT and BAT. Moreover, Sections 304(c) and 306 of the Act required promulgation of regulations for NSPS, and Sections 304(f), 307(b), and 307(c) required promulgation of regulations for pretreatment standards. In addition to these regulations for designated industry categories, Section 307(a) of the Act required the Administrator to develop a list of toxic pollutants and promulgate effluent standards applicable to all dischargers of toxic pollutants. Finally, Section 501(a) of the Act authorized the Administrator to prescribe any additional regulations "necessary to carry out his functions" under the Act.

The EPA was unable to promulgate many of these regulations by the dates contained in the Act. In 1976, EPA was sued by several environmental groups, and in settlement of this lawsuit EPA and the plaintiffs executed a "Settlement Agreement" which was approved by the Court. This Agreement required EPA to develop a program and adhere to a schedule for promulgating BAT effluent limitations guidelines, pretreatment standards, and new source performance standards for 65 "priority" pollutants and classes of pollutants for 21 major industries. See Natural Resources Defense Council, Inc. v. Train, 8 ERC 2120 (D.D.C. 1976), modified 12 ERC 1833 (D.D.C. 1979).

On December 27, 1977, the President signed into law the Clean Water Act of 1977. Although this law makes several important changes in the federal water pollution control program, its most significant feature is its incorporation of several of the basic elements of the Settlement Agreement program for toxic pollution control. Sections 301(b)(2)(A) and 301(b)(2)(C) of the Act now require the achievement by July 1, 1984 of effluent limitations requiring application of BAT for "toxic" pollutants, including the 65 "priority" pollutants and classes of pollutants which Congress declared "toxic" under Section 307(a) of the Act. Likewise, EPA's programs for new source performance standards and pretreatment standards are now aimed principally at toxic pollutant controls. Moreover, to strengthen the toxics control program, Section 304(e) of the Act authorizes the Administrator to prescribe "best management practices" ("BMPs") to prevent the release of toxic and hazardous pollutants from plant site runoff, spillage or leaks, sludge or waste disposal, and drainage from raw material storage associated with, or ancillary to, the manufacturing or treatment process.

In keeping with its emphasis on toxic pollutants, the Clean Water Act of 1977 also revises the control program for non-toxic pollutants. Instead of BAT for "conventional" pollutants identified under Section 304(a)(4) (including biochemical oxygen demand, suspended solids, fecal coliform and pH), the new Section

301(b)(2)(E) requires achievement by July 1, 1984, of "effluent limitations requiring the application of the best conventional pollutant control technology" ("BCT"). The factors considered in assessing BCT for an industry include a cost-reasonableness test for attaining a reduction in effluents compared to the costs incurred by a publicly owned treatment works (Section 304(b)(4)(B)). This is determined by an analysis of the reasonableness of the costs of attaining a reduction in effluents and the effluent pollutant reduction benefits derived, and the comparison of the cost and level of reduction of such pollutants from the discharge of publicly owned treatment works to the cost and level of reduction of such pollutants from a class or category of industrial sources. For non-toxic, nonconventional pollutants, Sections 301(b)(2)(A) and (b)(2)(F) require achievement of BAT effluent limitations within three years after their establishment or by July 1, 1984, whichever is later, but not later than July 1, 1987.

The purpose of these regulations is to provide effluent limitations guidelines for BPT, BAT, and BCT, and to establish NSPS, pretreatment standards for existing sources (PSES), and pretreatment standards for new sources (PSNS), under Sections 301, 304, 306, 307, and 501 of the Clean Water Act.

The United States Environmental Protection Agency (the Agency) was entrusted with the responsibility to carry out the requirements of the Act, and initiated an intensive effort to develop the necessary regulatory means which would achieve the stepwise reduction and elimination of pollutant discharges in all major U.S. industries. For the Inorganic Chemicals Manufacturing Point Source Category, the Agency designed a comprehensive, two-stage program to identify the control parameters and establish the technological basis for regulations development. Stage I covered 22 Major Inorganic Chemical Products (1), and the final regulations for these industrial subcategories were published in the Federal Register on March 12, 1974. The regulations included specific numerical effluent limitations and standards of performance for both existing and new sources. Zero-discharge requirements specified for many of the subcategories were to be applied either at the 1977 BPT step or later. Stage II of the Agency's effort resulted in the promulgation of BPT based effluent limitations for an additional group of 27 subcategories referred to as Significant Inorganic Chemical Products (2). The interim final regulations were published on May 22, 1975. Taken together, the two groups of regulations cover 49 inorganic chemical subcategories many of which include more than one specific chemical product. Although some toxic pollutants were covered in cases where a direct relationship to the process was obvious (e.g., mercury and/or lead in the Chlor-Alkali Industry), the main thrust of the regulations was the control of the pollutant parameters which accounted, in terms of quantity, for most of the pollution loading of navigable waters attributable to the manufacture of inorganic chemicals.

Court Remand of Regulations

On March 10, 1976, the United States Court of Appeals for the Fourth Circuit in E. I. duPont de Nemours & Co. v. Train, 541 F.2d 1018 (4th Cir. 1976), set aside and remanded for reconsideration a number of general definitions and specific discharge regulations promulgated in 1974. These regulations were all within Title 40, Parts 401 and 415 of the Code of Federal Regulations and covered the chlor-alkali, hydrochloric acid, hydrofluoric acid, nitric acid, sodium carbonate, sodium dichromate, sodium metal, sodium silicate, sulfuric acid, and titanium dioxide subcategories.

For the most part, the main target of the remand was zero discharge regulations from which the industry petitioners sought relief on grounds of technological infeasibility. During 1975, the Agency funded a special study of the remand issues (3) and was prepared to propose amended regulations.

Following the court remand of the stage I final regulations, the Agency revoked the stage II interim final and proposed regulations published in May 1975, for Aluminum Fluoride, Chrome Pigments, Hydrogen Cyanide, and Sodium Silicofluoride. In this instance, the Agency's intent was to reconsider the specific BPT effluent limitations established for these industries in the light of information made available on process differences between plants and additional data on the actual concentrations and treatability of the regulated discharge constituents. The information was presented to the Agency in the form of various documents prepared by members of the industries concerned (4).

The Settlement Agreement

A consent decree was issued as a result of a suit filed by four environmental groups (Natural Resources Defense Council, Inc. v. Train, 8 ERC 2120 (D.D.C. 1976), modified 12 ERC 1833 (D.D.C. 1979). The consent decree contained a Settlement Agreement wherein the Agency agreed to regulate 65 toxic pollutants under Sections 301, 304, 306, and 307 of the Act in accordance with the schedule and provisions stipulated. The original list of 65 chemicals and classes of chemicals attached to the Settlement Agreement was redefined to cover 129 chemical substances, including specific organic compounds, pesticides and their metabolites, polychlorinated biphenyls (PCB's), cyanide, 13 heavy metals and asbestos. Table 3-1 lists the 129 toxic pollutants (sometimes referred to in the literature as "priority pollutants").

The Settlement Agreement also identified 21 point source categories and specified the scope of application of effluent limitations, new source performance standards, and pretreatment standards within each category in terms of the Standard Industrial Classification (SIC) code numbers. For the Inorganic Chemicals Manufacturing Point Source Category, the major industries included are:

SIC 2812 - Alkalies and Chlorine
SIC 2813 - Industrial Gases
SIC 2816 - Inorganic Pigments
SIC 2819 - Industrial Inorganic Chemicals,
Not Elsewhere Classified

Phase I of the regulatory effort conducted in connection with the Inorganic Chemicals Point Source Category covered 60 of 177 subcategories previously identified as belonging to the category. The Phase I regulations were promulgated June 29, 1982 (47 FR 28260). Phase II was to have covered the remaining 117 subcategories. However, after review of all of the inorganic products listed in SIC codes 2812, 2813, 2816 and 2819, seven more subcategories were identified bringing the total number of subcategories examined in Phase II to 124. These additional subcategories were identified as the result of contacts with chemical producers, a literature search, site visits by EPA and contractor personnel, and telephone communications. Of the 124 subcategories, 107 were excluded from further study for the following reasons (See Section 19 - Excluded Subcategories):

1. The chemical is no longer being produced;
2. Only one plant was known to be producing the chemical;
3. Production quantities were low (below 4.5 kkg/yr (<10,000 lb/yr));
4. No dischargers could be identified in the subcategory;
5. No toxic pollutants were found at significant treatable levels;
6. The subcategories were already regulated by existing guidelines; or
7. One subcategory will be covered in a future rulemaking in another category.

Phase II Inorganic Chemicals

TABLE 3-1
LIST OF TOXIC POLLUTANTS

1. Acenaphthene
2. Acrolein
3. Acrylonitrile
4. Benzene
5. Benzidine
6. Carbon Tetrachloride
   (Tetrachloromethane)
7. Chlorobenzene
8. 1,2,4-Trichlorobenzene
9. Hexachlorobenzene
10. 1,2-Dichloroethane
11. 1,1,1-Trichloroethane
12. Hexachloroethane
13. 1,1-Dichloroethane
14. 1,1,2-Trichloroethane
15. 1,1,2,2-Tetrachloroethane
16. Chloroethane
17. Bis(Chloromethyl)Ether(1)
18. Bis(2-Chloroethyl)Ether
19. 2-Chloroethyl Vinyl Ether (Mixed)
20. 2-Chloronaphthalene
21. 2,4,6-Trichlorophenol
22. Parachlorometa Cresol
23. Chloroform (Trichloromethane)
24. 2-Chlorophenol
25. 1,2-Dichlorobenzene
26. 1,3-Dichlorobenzene
27. 1,4-Dichlorobenzene
28. 3,3'-Dichlorobenzidine
29. 1,1-Dichloroethylene
30. 1,2-Trans-Dichloroethylene
31. 2,4-Dichlorophenol
32. 1,2-Dichloropropane
33. 1,2-Dichloropropylene
   (1,3-Dichloropropene)
34. 2,4-Dimethylphenol
35. 2,4-Dinitrotoluene
36. 2,6-Dinitrotoluene
37. 1,2-Diphenylhydrazine
38. Ethylbenzene
39. Fluoranthene
40. 4-Chlorophenyl Phenyl Ether
41. 4-Bromophenyl Phenyl Ether
42. Bis(2-Chloroisopropyl) Ether
43. Bis(2-Chloroethoxy)Methane
44. Methylene Chloride
45. Methyl Chloride (Chloromethane)
46. Methyl Bromide (Bromomethane)
47. Bromoform (Tribromomethane)
48. Dichlorobromoethane
49. Trichlorofluoromethane(2)
50. Dichlorodifluoromethane(2)
51. Chlorodibromomethane
52. Hexachlorobutadiene
53. Hexachlorocyclopentadiene
54. Isophorone
55. Naphthalene
56. Nitrobenzene
57. 2-Nitrophenol
58. 4-Nitrophenol
59. 2,4-Dinitrophenol
60. 4,6-Dinitro-O-Cresol
61. N-Nitrosodimethylamine
62. N-Nitrosodiphenylamine
63. N-Nitrosodi-N-Propylamine
64. Pentachlorophenol
65. Phenol
66. Bis(2-ethylhexyl)Phthalate
67. Butyl Benzyl Phthalate
68. Di-N-Butyl Phthalate
69. Di-N-Octyl Phthalate
70. Diethyl Phthalate
71. Dimethyl Phthalate
72. 1,2-Benzanthracene (Benzo(A)Anthracene)
73. Benzo (A) Pyrene (3,4-Benzo-Pyrene)
74. 3,4-Benzofluoranthene (Benzo(B)
   (Fluoranthene)
75. 11,12-Benzofluoranthene (Benzo(K)
   Fluoranthene)
76. Chrysene
77. Acenaphthylene
78. Anthracene
79. 1,12-Benzoperylene(Benzo(GHI)-Perylene)
80. Fluorene
81. Phenanthrene
82. 1,2,5,6-Dibenzathracene(Dibenzo(A,H)
   Anthracene)
83. Ideno(1,2,3-CD)Pyrene(2,3-O-Phenylene
   Pyrene)
84. Pyrene
85. Tetrachloroethylene
86. Toluene
87. Trichloroethylene
88. Vinyl Chloride (Chloroethylene)
89. Aldrin
90. Dieldrin
91. Chlordane (Technical
   Mixture and Metabolites)
92. 4,4'-DDT
93. 4,4'-DDE (P,P'-DDX)
94. 4,4'-DDD (P,P-TDE)
95. Alpha-Endolsufan
96. Beta-Endosulfan
97. Endosulfan Sulfate
98. Endrin
99. Endrin Aldehyde
100. Heptachlor
101. Heptachlor Epoxide (BHC-
   Hexachlorocyclohexane)
102. Alpha-BHC
103. Beta-BHC
104. Gamma-BHC
105. Delta-BHC
106. PCB-1242 (Arochlor 1242)
107. PCB-1254 (Arochlor 1254)
108. PCB-1221 (Arochlor 1221)
109. PCB-1232 (Arochlor 1232)
110. PCB-1248 (Arochlor 1248)
111. PCB-1260 (Arochlor 1260)
112. PCB-1016 (Arochlor 1016)
113. Toxaphene
114. Antimony
115. Arsenic
116. Asbestos
117. Beryllium
118. Cadmium
119. Chromium
120. Copper
121. Cyanide
122. Lead
123. Mercury
124. Nickel
125. Selenium
126. Silver
127. Thallium
128. Zinc
129. 2,3,4,8-Tetrachlorodibenzo-
   P-Dioxin (TCDD)

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(1) Deleted 02/04/81; 46 FR 10723
(2) Deletec 01/08/81; 46 FR 2266

The Agency identified 17 chemical products in Phase II for which effluent limitations guidelines and standards are warranted. Engineering and sampling visits were conducted and a comprehensive data gathering program was undertaken in order to complete this effort. This report documents the Agency's findings with respect to the list of 17 chemical products identified in Table 3-2.

TABLE 3-2. CHEMICAL PRODUCTS COVERED UNDER THE PHASE II STUDY

1. Cadmium Pigments
2. Cadmium Chloride
3. Cadmium Nitrate
4. Cadmium Sulfate
5. Cobalt Chloride
6. Cobalt Nitrate
7. Cobalt Sulfate
8. Copper Carbonate
9. Copper Chloride
10. Copper Iodide
11. Copper Nitrate
12. Nickel Carbonate
13. Nickel Chloride
14. Nickel Fluoborate
15. Nickel Nitrate
16. Sodium Chlorate
17. Zinc Chloride

On October 25, 1983, the Agency proposed effluent limitations and standards for the above subcategories (48 FR 49408) as well as amended limitations and standards for sodium chloride and sodium sulfite. This document is a revised version of the supporting development document for that proposal.

GENERAL APPROACH AND METHODOLOGY

Initiating and undertaking a comprehensive study of the toxic pollutant problem in the Inorganic Chemicals Industry was preceded by an intensive evaluation by the Agency of the kinds of data and supporting information that should be assembled as a basis for the development of regulations. All major decisions on the identity of pollutants and the establishment of effluent limitations and standards of performance for each subcategory had to be supportable by documented evidence collected from operating production facilities. Similarly, the necessary information on production rates, processes, raw materials, water use, waste sources, and treatment technologies in practice had to be acquired with sufficient detail and breadth of coverage to permit an analysis of the engineering and economic variables that are characteristic of each subcategory. Toxic pollutant control regulations would be based on the application of best available technology for treatment and reliable performance evaluations for the removal of specific waste substances.

The following paragraphs briefly describe the major study tasks and their results as they are presented in this report.

Industry Data Base Development and Subcategorization Review

Information from individual manufacturers and previous study documents were reviewed in detail and an evaluation of possible subcategorization was performed. A review of the data base acquired for this group of chemical products indicated that there are 46 individual facilities in this group (many plants are multiple product plants). The Agency has data submitted by industry in response to requests for information under Section 308 of the Act (obtained during Phase I or II) or engineering visit data on file for 44 of the 46 plants. In addition, EPA obtained data from State agencies, Regional offices, compliance visits by the States, telephone contacts, and letter requests. During screening and verification sampling, 13 plants were sampled. EPA conducted additional engineering visits during October and November 1982 to twelve plants (three had been visited previously during the sampling program). Section 4 outlines the factors considered in subcategorization and presents the rationale for the proposed scheme of subcategorization for the 17 chemical products studied. Final subcategorization is identical to the proposed subcategorization of October 25, 1983.

The Screening and Verification Sampling Program

The collection of detailed analytical data on conventional, nonconventional and toxic pollutant concentrations in raw and treated process wastewater streams was completed in a comprehensive sampling program. The sampling and analytical methodology is described in Section 5. The Phase I study showed that organic priority pollutants would not be expected to be significant in this industry group. Therefore, the screening and verification sampling program was modified to reduce the frequency of organic sampling for Phase II. This sampling program is described in detail in Section 5. In all, 13 of the 46 plants were sampled during the sampling program.

Engineering Evaluation

Section 6 describes the procedures and sources used in developing the industry production and wastewater generation characteristics that form the basis of the model plant concept. The sources of detailed process and waste treatment information are also presented. Section 7 contains an evaluation of treatment technology presently applied in existing wastewater treatment systems and advanced technologies that may be recommended for BAT and NSPS applications. Section 8 provides estimates of the treatability of selected toxic and nonconventional pollutants to be applied in the development of achievable performance characteristics for specific technologies. Section 8 also presents a discussion of the approach taken in the statistical analysis of long-term monitoring data. The statistically derived parameters, including variability factors for the 24-hour maximum and maximum 30-day average limitations, are presented in Appendix A. Section 9 lays the groundwork for the estimation of pollutant removal performances for each subcategory. The candidate toxic pollutants to be controlled in each subcategory are identified on the basis of the screening and verification data and the rationale for the application of advanced level technologies is presented.

Treatment System Cost Estimates

Section 10 presents the general approach to cost estimating, discusses the assumptions made, and gives the detailed cost estimates for alternative levels of treatment and control. For each subcategory, the total estimated installed cost of typical treatment systems is developed on the basis of model plant design specifications. Estimated incremental costs are given for each of the advanced level treatment alternatives. Estimates of the sludge generated by treatment and the costs associated with their proper disposal in compliance with anticipated RCRA requirements are included (based upon evaluation of EP toxicity data). Where available, industry data on sludge volumes and characteristics were utilized. Disposal costs were estimated on the basis of disposal in an off-site hazardous material landfill (except where noted).

Treatability Studies

Data was collected through a treatability study in Phase I (4) to evaluate the achievable performance of various treatment and control alternatives and to provide empirical treatment system performance information applicable to selected inorganic chemical subcategories. The study, completed in July 1980, specifically concentrated on those subcategories in the Phase I Inorganic Chemicals Industry for which treatability data either did not exist or was deficient, and for which data were needed for purposes of comparison with proposed effluent limitations for those Phase I subcategories. Subcategories of Phase I for which treatability studies were conducted include:

Nickel sulfate
Hydrofluoric acid
Copper sulfate
Chlor-alkali (diaphragm cells)
Titanium dioxide (chloride process)
Chrome pigments
Sodium dichromate

Sodium bisulfite
Sodium hydrosulfite

This treatability study is relevant to Phase II because the chemical manufacturing processes are similar, similar wastewater treatment practices are employed, and similar wastewater streams have been encountered.

In order to evaluate the effectiveness of filtration technology on zinc chloride process wastewaters, a treatability study was also performed at a zinc chloride manufacturing facility in 1984(5). This study established the relationship between total and dissolved zinc as well as the effectiveness of the treatment for removal of TSS, turbidity, total and dissolved zinc, arsenic and lead. The results of this study are summarized in Section 16.

Where adequate data were unavailable for Phase II, treatability study results for similar wastewater streams from Phase I and other industries were taken into account in determination of achievable levels of performance.

GENERAL CRITERIA FOR EFFLUENT LIMTATIONS

BPT Effluent Limitations

The factors considered in defining best practicable control technology currently available (BPT) include the total cost of applying such technology in relation to the effluent reductions derived from such application, the age of equipment and facilities involved, the process employed, non-water quality environmental impacts (including energy requirements), and other factors the Administrator considers appropriate (Section 304(b)(1)(B)). In general, the BPT technology level represents the average of the best existing performances of plants of various ages, sizes, processes, or other common characteristics. Where existing performance is uniformly inadequate, BPT may be transferred from a different subcategory or category. BPT focuses on end-of-pipe treatment rather than process changes or internal controls, except where such are common industry practice. The cost/benefit inquiry for BPT is a limited balancing, committed to EPA's discretion, which does not require the Agency to quantify benefits in monetary terms. See, e.g., American Iron and Steel Institute v. EPA, 526 F.2d 1027 (3rd Cir. 1975). In balancing costs in relation to effluent reduction benefits, EPA considers the volume and nature of existing discharges, the volume and nature of discharges expected after application of BPT, the general environmental effects of the pollutants, and the cost and economic impacts of the required pollution control level. The Act does not require or permit consideration of water quality problems attributable to particular point sources or industries, or water quality improvements in particular water bodies. Therefore, EPA has not considered these factors. See Weyerhaeuser Co. v. Costle, 590 F.2d 1011 (D.C. Cir. 1978).

BAT Effluent Limitations

The factors considered in assessing best available technology economically achievable (BAT) include the age of equipment and facilities involved, the process employed, process changes, and non-water quality environmental impacts (including energy requirements), (Section 304(b)(2)(B)). At a minimum, the BAT technology level represents the best economically achievable performance of plants of various ages, sizes, processes, or other shared characteristics. As with BPT, uniformly inadequate performance may require transfer of BAT from a different subcategory or category. BAT may include process changes or internal controls, even when these technologies are not common industry practice. The statutory assessment of BAT "considers" costs, but does not require a balancing of costs against effluent reduction benefits (see Weyerhaeuser v. Costle, supra). In developing the BAT regulations, however, EPA has given substantial weight to the reasonableness of costs. The Agency has considered the volume and nature of discharges, the volume and nature of discharges expected after application of BAT, the general environmental effects of the pollutants, and the costs and economic impacts of the required pollution control levels. Despite this expanded consideration of costs, the primary determinant of BAT is effluent reduction capability. As a result of the Clean Water Act of 1977, 33 USC 1251 *et seq*., the achievement of BAT has become the principal national means of controlling water pollution due to toxic pollutants.

BCT Effluent Limitations

The 1977 amendments added Section 301(b)(2)(E) to the Act, establishing "best conventional pollutant control technology" (BCT) for discharges of conventional pollutants from existing industrial point sources. Conventional pollutants are those defined in Section 304(b)(4) - BOD, TSS, fecal coliform, and pH. Oil and grease was designated by the Administrator as "conventional" on July 30, 1979, 44 FR 44501. BCT is not an additional limitation, but replaces BAT for the control of conventional pollutants

Section 304(b)(4)(B) of the Act requires that BCT limitations be assessed in light of a two part "cost reasonableness" test, American Paper Institute v. EPA 660 F.2d 954 (4th Cir. 1981). The first test compares the cost for private industry to reduce its conventional pollutants with the costs to publicly owned treatment works for similar levels of reduction in their discharge of these pollutants. The second test examines the cost-effectiveness of additional industrial treatment beyond BPT. EPA must find that limitations are "reasonable" under both tests before establishing them as BCT. In no case may BCT be less stringent than BPT. EPA published its methodology for carrying out the BCT analysis on August 29, 1979 (44 FR 50732). However, the cost test was remanded by the United States Court of Appeals for the Fourth Circuit. American Paper Institute v. EPA, 660 F.2d 954 (4th Cir. 1981). The Court of Appeals ordered EPA to correct data errors underlying EPA's calculation of the first test, and to apply the second cost test. (EPA had argued that a second cost test was not required). The Agency proposed a revised BCT methodology October 29, 1982 (47 FR 49176).

New Source Performance Standards

The basis for new source performance standards (NSPS) under Section 306 of the Act is the best available demonstrated technology. New plants have the opportunity to design the best and most efficient inorganic chemicals manufacturing processes and wastewater treatment technologies, and Congress therefore directed EPA to consider the best demonstrated process changes, in-plant controls, and end-of-pipe treatment technologies which reduce pollution to the maximum extent feasible.

Pretreatment Standards for Existing Sources

Section 307(b) of the Act requires EPA to promulgate pretreatment standards for existing sources (PSES) which must be achieved within three years of promulgation. PSES are designed to prevent the discharge of pollutants which pass through, interfere with, or are otherwise incompatible with the operation of POTWs. The Clean Water Act of 1977 adds a new dimension by requiring pretreatment for pollutants, such as toxic metals, that limit POTW sludge management alternatives, including the beneficial use of sludges on agricultural lands. Pretreatment is required for toxic pollutants that would pass through a POTW in amounts that would violate direct discharger effluent limitations. EPA has generally determined that there is pass through of pollutants if the percent of pollutants removed by a well-operated POTW achieving secondary treatment is less than the percent removed by the BAT model treatment system. The legislative history of the 1977 Act indicates that pretreatment standards are to be technology-based, analogous to the best available technology for removal of toxic polltuants. The general pretreatment regulations which served as the framework for these pretreatment regulations can be found in 40 CFR Part 403, 46 FR 9409 (January 28, 1981); 47 FR 42688 and 47 FR 42698 (Sept. 28, 1982).

Pretreatment Standards for New Sources

Section 307(c) of the Act requires EPA to promulgate pretreatment standards for new sources (PSNS) at the same time that it promulgates NSPS. New indirect dischargers, like new direct dischargers, have the opportunity to incorporate the best available demonstrated technologies including process changes, in-plant controls, and end-of-pipe treatment technologies, and to use plant site selection to ensure adequate treatment system installation.

SECTION 3

REFERENCES

1. U.S. Environmental Protection Agency, Major Inorganic Products, Development Document. EPA-440/1-74-007a, 1974.

2. U.S. Environmental Protection Agency, Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Significant Inorganic Products, EPA-440/1-75-037, 1975. 358 pp.

3. Calspan Corp. Addendum to Development document for Effluent Limitations Guidelines and New Source Performance Standards, Major Inorganic Products Segment of Inorganic Chemicals Manufacturing Point source Category, Contract No. 68-01-3281, 1978.

4. U.S. Environmental Protection Agency, Development Document for Final Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-82/007, June 1982.

5. Harty, D.M., Funke, D.M., and Terlecky, P.M., "Dual-Media Filtration Treatability Test Results at Zinc Chloride Plant F144," Report No. FTA-84-E6-01, Frontier Technical Associates, Buffalo, N.Y., May 1984.

SECTION 4

SUBCATEGORIZATION

Basis for Subcategorization

Factors Considered

The inorganic chemicals industry is very large and diversified and has been segmented into subcategories for the purpose of establishing effluent guidelines. Factors taken into consideration for subcategorization include: raw materials used, product produced, manufacturing process employed, geographical location, size and age of equipment and facility involved, non-water-quality aspects of waste characteristics, water pollution control technology, treatment costs, energy requirements and solid waste disposal. Following is a discussion of each of the general factors considered for this industry.

Raw Materials

Different raw materials are used to manufacture a wide variety of products, and vary from raw brines and ores to pure reagent chemicals. Some processes use waste or by-product streams from other plants or from other processes within the same plant.

Because of this diversification, raw material characteristics generally do not constitute a logical basis for subcategorization. Variations in raw material quality or purity are not normally sufficient to cause a great difference in wastewater treatment needs, except in the case of trace toxic materials which may occur in some sources but not in others.

Dominant Product

Subcategorization by chemical name of the dominant inorganic chemical produced involves the least ambiguity in applying standards to a given point source. This is critical because of the great variety of product mix, manufacturing processes, wastewater constituents, and other factors at existing plants. Subcategorization by product becomes less useful as product mix increases in complexity because multi-product wastewater also becomes more complex and less susceptible to simple uniform treatment.

A subcategory established on the basis of product manufactured might have two or more different processes but, in the majority of cases, the characteristics of the wastewaters are similar and the same treatment technology can be applied for different process wastewaters. If two or more dissimilar processes produce wastewater of different quality, and different treatment technologies have to be used, then the subcategory may be further classified or segmented.

Manufacturing Process

Typically, inorganic chemicals are manufactured for captive or merchant use in four or more steps starting from raw material to final product. Two or more different products might use the same process but then the raw materials used, process sequence, control, recycle potential, handling, and quality control will vary, producing wastes of different quality. Primary subcategorization, therefore, by process is unlikely to be useful. However, secondary subcategorization by process may be necessary in some cases.

Geographical Location

Inorganic chemical plants exist in all parts of the United States but subcategorization on this basis is not appropriate. Geographical location is important in analyzing the feasibility of various treatment alternatives. Evaporation ponds are functional only in areas where evaporation exceeds rainfall. Ocean dumping and deep well disposal are possible only in certain areas, and must be consistent with local, state and federal laws. The possibility of ground water contamination may preclude the use of unlined holding and settling ponds in many locations.

In the northern regions, climatic conditions may necessitate the inclusion of special provisions to prevent freezing of treatment system components, particularly biological oxidation units, clarifiers, ponds, and open collection systems. The costs of utilizing waste heat sources from the process or providing various types of thermal protection, such as insulation or burial of pipes and tanks and building structural shelters, may add considerably to the capital and O&M cost associated with a treatment technology.

Thus, the influence of geography, climate, geology, etc., is reflected in wastewater treatment modifications and is primarily manifested in the cost of treatment. This, of itself, is not a good basis for subcategorization.

Plant Size

Plant size and production capacity were not found to affect the characteristics of the wastewater produced. Although plant size can affect treatment cost, this variability can be expressed graphically or mathematically without the need for further segmentation of the category.

Plant Age

Plant age can have an important bearing on wastewater volume and quality and is, therefore, a significant factor to consider in evaluating the applicability of treatment technologies and assessing the relative costs of treatment for plants of widely differing age producing the same or similar products. A particular problem with older plants is that their present patterns of water use may have evolved over a long period of time with little consideration for the principles of efficient waste segregation, collection, and treatment. To a limited degree, plant modernization can correct or at least mitigate some of these shortcomings in older facilities, however, only a small proportion of the cost of revamping collection systems or of converting from contact to noncontact cooling systems can be offset by the resulting lower cost of treatment. In general, older plants, even after considerable modernization, normally have a higher volume of wastewater flow and higher waste loadings (although pollutant concentrations may be lower due to poor segregation from noncontact sources) in comparison to relatively new plants. Pollution control requirements could impose a severe treatment cost penalty on older plants due to the need for backfitting and replumbing of outdated collection systems. Land availability and land use restrictions are also factors which may translate into higher treatment costs for older facilities which find themselves surrounded by highly developed industrial and residential areas.

Unfortunately, plant age does not readily lend itself to an unambiguous definition where a series of plant modifications has taken place. The extent of modifications also varies greatly among plants within the same product industry. For those plants that have been enlarged or modified from their original status, plant age is not unambiguously calculable and therefore is not a reasonable basis for subcategorization.

Non-Water-Quality Characteristics

Airborne emissions from manufacturing operations can be kept within air quality control limits through the use of cyclones, wet scrubbers and other methods. The nature of the air pollution is related to the product(s) manufactured and/or the raw material used. Since both of these elements vary widely within the inorganic chemicals industry, there is no logic in subcategorization on the basis of non-water-quality characteristics.

Treatment Cost

From a technical viewpoint, subcategorization by common technological requirements for treatment processes could provide a logical basis for selecting one or more unit processes to accomplish the same treatment function, regardless of the source of the wastewater. For example, residuals of dissolved heavy metals will respond to lime precipitation and sedimentation at high pH without respect to the specific origin of the metals. This "building block" concept could conceivably result in selecting various combinations of unit processes to meet the treatment requirements. However, if the treatment cost must be expressed in terms of dollars per unit production, this method of subcategorization crosses product lines and interferes with comparison of treatment costs based on the production of a specific chemical. Even if the unit operation is commonly applicable for treating wastewater flows of different products, the cost of treatment will fluctuate because of variations in wastewater quality, loading and flow rates, and subcategorization on the basis of treatment cost is not recommended.

Energy Cost

Manufacturing processes in the Inorganic Chemicals Industry typically have large energy requirements. In contrast, wastewater treatment processes consume a small fraction of the total energy used. There appears to be no major energy requirements for wastewater treatment facilities, therefore subcategorization on the basis of energy cost is not justified.

Solid Waste

Not all inorganic manufacturing processes produce solid wastes. Solid waste producers practice various disposal methods, such as on-site landfills, contract hauling to approved disposal sites, or incineration. Solid waste disposal becomes very site specific and exhibits a wide range of costs. Because of the lack of uniformity within the industry, solid waste generation and disposal practices are not a satisfactory basis for subcategorization.

General Conclusions

If effluent limitations are to be tied to effluent concentrations or units of production, only one method of primary subcategorization is broadly applicable to the inorganic chemicals point source category, namely subdivision by dominant product. Within the seventeen chemicals studied, it was determined that wastewater characteristics were more dependent upon the cation (metal) involved than the anionic species. Many processes within a group of compounds were found to be basically similar and wastewater treatment processes expected to be used would be similar. In fact, at many plants, many of the products were produced utilizing batch processes (e.g., copper carbonate, copper sulfate, and copper nitrate may be produced at the same plant at different times). Wastewater treatment process design at these plants focuses on treatment of dissolved and particulate metals, TSS, and pH. These treatment plants must be capable of performance with a variety of wastewater streams.

From a cost standpoint, most plants in the Phase II chemicals group will not be impacted in the same way as many large, single product plants in Phase I because the treatment costs incurred can be allocated to a large variety of products at the plants, not just a single product or product group. Therefore costs expressed in this document may overstate the actual costs to be incurred.

To allow a workable subcategorization scheme, the factors described earlier were considered and the following subcategorization scheme is recommended:

I. Cadmium Pigments and Salts

II. Cobalt Salts

III. Copper Salts

IV. Nickel Salts

V. Sodium Chlorate

VI. Zinc Chloride

It is recommended that separate effluent limitations and standards be promulgated for each of the six groups listed above. This subcategorization allows separate limitations to be established within groups of chemicals whose wastewater is basically similar, employ similar processes and raw materials and would be expected to utilize similar or identical wastewater treatment within the subcategory.

Chemicals Covered. It is recommended, therefore, that the seventeen chemicals considered in Phase II be subdivided as follows:

I. Cadmium Pigments and Salts

  - A. Cadmium Pigments
  - B. Cadmium Chloride
  - C. Cadmium Nitrate
  - D. Cadmium Sulfate

II. Cobalt Salts

  - A. Cobalt Chloride
  - B. Cobalt Nitrate
  - C. Cobalt Sulfate

III. Copper Salts

  - A. Copper Carbonate
  - B. Copper Chloride
  - C. Copper Iodide
  - D. Copper Nitrate

The Copper Salts subcategory also includes Copper Sulfate.

IV. Nickel Salts

  - A. Nickel Carbonate
  - B. Nickel Chloride
  - C. Nickel Fluoborate
  - D. Nickel Nitrate

The Nickel Salts subcategory also includes Nickel Sulfate.

V. Sodium Chlorate

VI. Zinc Chloride

EPA is replacing two subcategories with new consolidated subcategories. Subpart AJ (Copper Sulfate) is replaced by Subpart AJ (Copper Salts) which includes copper sulfate, copper chloride, copper iodide, copper nitrate, and copper carbonate. Subpart AU (Nickel Sulfate) is replaced by Subpart AU (Nickel Salts), which includes nickel sulfate, nickel chloride, nickel nitrate, nickel fluoborate, and nickel carbonate.
This subcategorization is used for the following reasons:

a. Many facilities produce copper sulfate or nickel sulfate as well as other copper or nickel salts covered in these subparts. The wastewater streams are typically commingled and sent to a common wastewater treatment system.

b. The production processes for copper or nickel sulfate and the other copper or nickel salts covered in this subpart are very similar.

c. Wastewater flows and pollutant characteristics are very similar for copper or nickel sulfate and the other copper or nickel salts.

d. Wastewater treatment processes which have been determined to be effective in the copper or nickel sulfate industry are the same as for the other salts.

e. Levels of treatability are the same for copper or nickel sulfate and the other copper or nickel salts.

The exception to the above is the copper or nickel carbonate production industry. Copper carbonate is a separate segment within the Copper Salts subcategory and nickel carbonate is a separate segment within the Nickel Salts Subcategory because the wastewater unit flows at copper carbonate and nickel carbonate facilities are substantially greater than at other copper or nickel salts facilities covered in these subparts.

The Agency is excluding 106 subcategories from regulation primarily because the discharges from all plants in the subcategory are insignificant. The Agency is also deferring regulation of one subcategory for coverage under another, more appropriate, point source category. The Agency first considered consolidating many of those subcategories by dominant metal to develop new larger subcategories. However, in many cases this consolidation was technically infeasible because the production process, water use, raw material, and expected pollutants were too dissimilar. In the remaining cases, the combined discharges from all plants in the consolidated subcategories are also insignificant and would therefore be proposed for exclusion. These cases are noted in Section 19 infra. Only the consolidations of the 17 subcategories just described above are both technically feasible and result in new subcategories with significant discharges. The Agency would have proposed exclusions for several of the nickel salts, copper salts, cobalt salts, and cadmium salts in the absence of this consolidation.

SECTION 5

SAMPLING PROGRAM

SCOPE AND METHODOLOGY

The specific objective of the sampling program was to establish the extent of the required regulation of toxic pollutant discharges in the inorganic chemicals industry in terms of factual information derived from the chemical analysis and flow measurement of representative process raw wastewater streams and treated effluents. Prior to this study, most of the information available on toxic pollutants has been concerned with a relatively small number of known process-related substances contaminating a variety of direct and indirect contact process waters discharged from a production facility. There had been no previous requirement for a comprehensive survey of wastewater chemistry addressing the possibility that a large number of other potentially toxic substances could be present, albeit at extremely low concentrations.

The sampling program was designed to ascertain the presence in each subcategory of any of the 129 listed toxic pollutants at raw waste concentrations or daily loadings which, if untreated, could be environmentally significant. The program was based on the sampling of one or more typical manufacturing operations in each subcategory to confirm and quantify the presence of toxic pollutants. (A goal was set for sampling of a sufficient number of plants to account for at least 20 percent of the total U.S. plants, in each subcategory.)

A detailed description of the sampling program is presented in the paragraphs below.

Selecting Plants and Making Preliminary Contacts

In each subcategory, plants were selected for sampling on the basis of the following general criteria:

A. Minimal product mix and no organic product lines which could increase the potential for interprocess cross contamination of wastewater;

B. Presence of a physical-chemical treatment facility rather than a biological one, or no treatment system;

C. Manufacture of industrial grade products in volume, rather than low volume reagent grade* products;

D. Median production capacity within the subcategory;

E. Segregated wastewater streams to facilitate sampling;

F. Direct discharges rather than discharges to POTWs were usually preferred, since treatment for a direct discharge is usually more extensive;

G. Geographical clustering of selected plants to facilitate field logistics, but only to the extent that other factors are equal.

*Chemicals produced of high purity, generally with production rates of less than 4.5 kkg/yr (<10,000 lb/yr).

Preliminary telephone contacts were made with plant representatives of those facilities which satisfied the above criteria. If requested, a letter was written to describe the objectives of the sampling program and to cite the legal authority of the Agency and its sampling contractor under Section 308 of the Act. Information provided by industry for which confidential treatment was requested has been handled in accordance with 40 CFR Part 2.

Prior to the actual sampling of wastewater streams, an engineering visit to the selected plant was made to gather background information and to obtain additional technical information regarding processes and wastewater treatment practices. The engineering visit information was often used as a sufficient response to the requests for information under Section 308 of the Act. (See Section 6). Sampling sites were selected and described relative to a detailed wastewater source inventory and a flow diagram of the process and wastewater treatment system. Arrangements were made for the subsequent sampling visit and the details of the engineering visit and sampling point descriptions were documented in an interim report to the Agency.

Sampling Program

A. Collection of Samples

In the sampling program, the specific objective was the detection and quantification of waterborne wastewater constituents included on the list of 129 toxic pollutants (Table 3-1). Each sample of an individual raw wastewater stream, a combined wastewater stream, or a treated effluent was collected where possible by an automatic, time series, compositor over a 72-hour sampling period (yielding three individual 24-hour composites). These samples were analyzed for the 13 toxic metal pollutants, cyanide and phenol, as well as the conventional and non-conventional pollutant paramaters associated with the particular subcategory. Where automatic compositing was not possible, grab samples were taken at approximately 2-hr intervals during the same sampling period and composited manually.

During one particular 24-hour composite period of the three days, samples were taken and analyzed for all 114 toxic organic pollutants and asbestos. The non-volatile organics were taken from the chosen daily composite sample while volatile organics and asbestos samples were collected as grab samples or grab composite samples.

Each sample was divided into several portions and preserved, as required for different types of analysis, in accordance with the procedure established by EPA (1) for the measurement of toxic pollutants.

Volatile organics were collected in teflon-sealed screw cap vials. Eight 40 ml vials were filled at each sampling site by grab sampling in pairs at approximately 2-hr intervals. The individual vials were cooled to 4°C and shipped to the laboratory where they were used to prepare composites in duplicate just prior to analysis. Three blank vials prepared and sealed in the laboratory accompanied each set of samples during collection, shipment and storage.

B. Sample Shipping

All samples, individually labeled, were placed in large plastic bags, which were then placed in a waterproof insulated shipping container. Enough ice was included to maintain a temperature of approximately four degrees C during shipment to the laboratory.

Containers were shipped by the best available route, usually air freight, usually arriving at the laboratory on the same day, but occasionally taking overnight. Upon receipt, all samples were immediately placed in a walk-in refrigerator maintained at 4°C.

In order to maintain the chain of custody and to maintain an account of samples, sampling personnel kept logs of samples taken in ink in page-numbered, hard-bound books. The data recorded included: date, time, plant code, number, sample type, and sampler. This information was also included on the label of individual samples. Prior to their arrival at the laboratory, a list of samples shipped, including number,

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type of samples, and analysis to be performed, was sent to each department supervisor to alert him of incoming work.

A master analytical control chart was maintained which included: date sample was received, date due, number and type of each sample, and the analysis required.

At the time of analysis, the individual samples were distributed to the analytical chemists along with a list which included: I.D. number of sample, type of sample, analysis required, date samples received, and due dates.

All samples were kept in a laboratory refrigerator at 4°C when not being handled by the analyst. Upon completion of analysis, the sample was checked back into the Sample Control Department and kept in an identified location in the Sample Control refrigerator. A report of completed samples was then sent to the EPA Sample Control Center.

Analytical Methodology for Toxic Pollutants

The protocol for the analysis of toxic pollutants was established in Sampling and Analysis Procedures for Priority Pollutants by U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, April 1977. The Agency subsequently proposed very similar methods on December 3, 1979 (44 FR 69464) under §304(h) of the Act. We used the proposed 304(h) methods of analysis for toxic organic pollutants and the promulgated 304(h) methods for analysis of toxic metals, conventional and non-conventional pollutants (40 CFR 136).

The specified analytical methodologies were employed without modification except where noted below in connection with toxic metals analysis.

Implementation of the methodology and quality assurance provisions required the establishment of special sample handling and control procedures specifically suited to each type of analysis. These procedures, together with a discussion of the achievable detection limits for each parameter or group of similar parameters are presented in the following paragraphs.

A. Trace Metal Analysis

Figure 5-1 shows a data flow diagram for metals analysis. Atomic absorption methods described in 40 CFR 136 per Section 304(h) were used. A set procedure was followed in the laboratory to generate the analytical values and the quality control data. The data flow diagram shows the

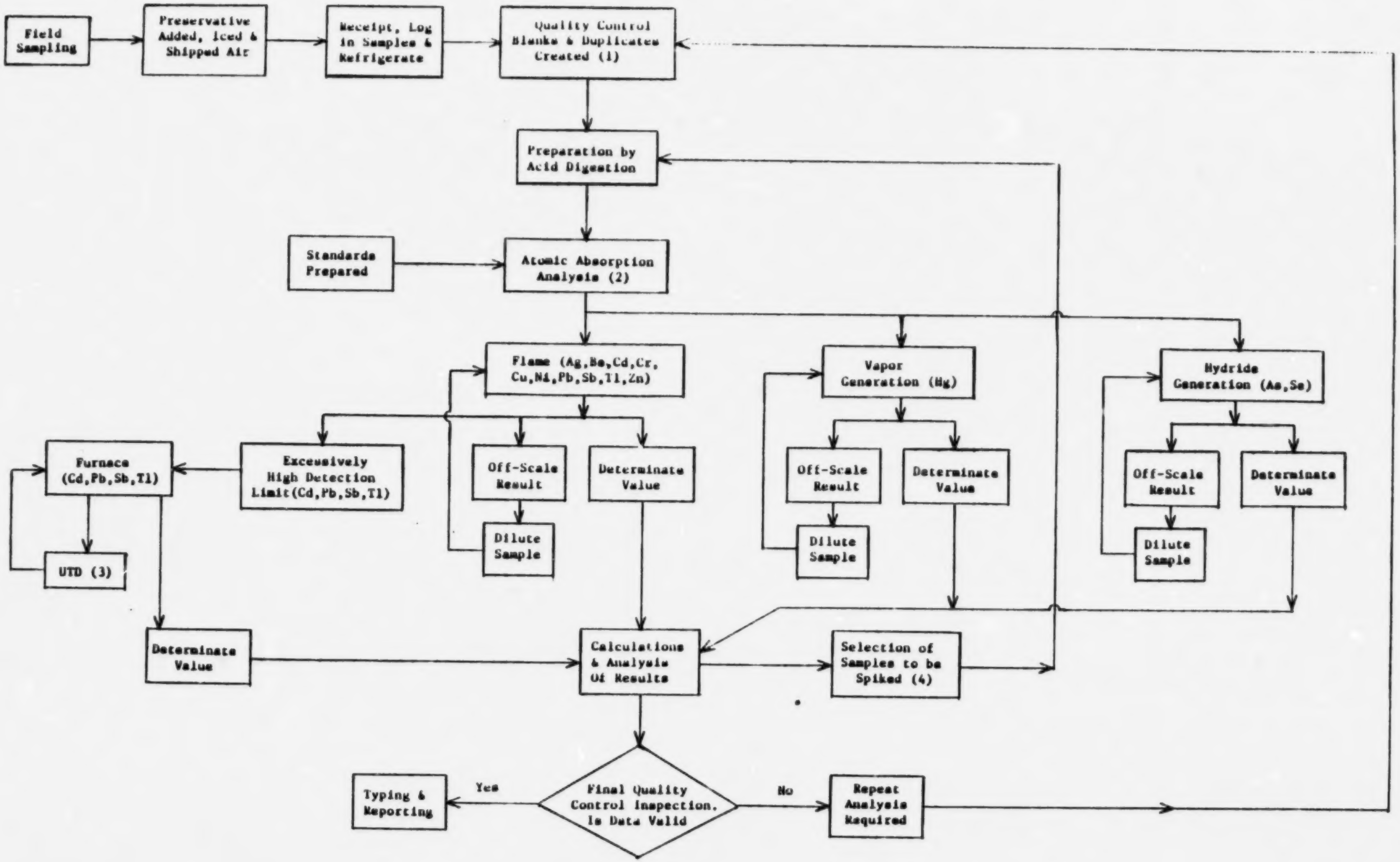
Field Sampling
Preservative Added, Iced & Shipped Air
Receipt, Log in Samples & Refrigerate
Quality Control Blanks & Duplicates Created (1)
Preparation by Acid Digestion
Standards Prepared
Atomic Absorption Analysis (2)
Flame (Ag,Be,Cd,Cr, Cu,Ni,Pb,Sb,Tl,Zn)
Vapor Generation (Hg)
Hydride Generation (As,Se)
Furnace (Cd,Pb,Sb,Tl)
Excessively High Detection Limit(Cd,Pb,Sb,Tl)
Off-Scale Result
Determinate Value
Off-Scale Result
Determinate Value
Off-Scale Result
Determinate Value
UTD (3)
Dilute Sample
Dilute Sample
Dilute Sample
Determinate Value
Calculations & Analysis Of Results
Selection of Samples to be Spiked (4)
Typing & Reporting
Yes
Final Quality Control Inspection. Is Data Valid
No
Repeat Analysis Required

FIGURE 5-1. SAMPLE FLOW SHEET FOR METAL ANALYSIS

actual sequence employed in the analytical program and the following notes, which are keyed to the diagram, provide additional information on the procedures:

1. Blanks -- two for each set of analyses digested. Duplicates -- one every seventh sample.

2. Quality Control at Operator Level (Atomic Absorption):

   Blanks - These were run at the beginning and the end of every set analyzed for each metal. Also, air blanks were run on furnace, or heated graphite atomizer, (HGA), after any sample with a large positive value.

   Standards - Three different concentrations were run at the beginning and end of every set analyzed for each metal. Standards were also run every tenth sample during the analysis of a set.

   Spikes - These were made according to the EPA "Method of Standard Additions," by adding such a volume of standard as to double the apparent concentration of metal present in the sample. Extrapolation backwards of the resultant absorbances allowed correction of absorbance for matrix effects.

   Duplicates - For furnace analysis, the sample was run twice wherever a low but positive absorbance was obtained. In addition, one sample in every seven was run in duplicate routinely. The average of duplicate measurements was the taken value; the difference between duplicate measurements was noted and recorded on control charts. If reproducibility was outside the limits of ±33 percent, the measurement was repeated.

3. UTD = "Unable To Determine" due to matrix interferences.

4. Criteria Employed in Spike Selection:

   a. Samples were chosen to be spiked based upon the following criteria:

      - All samples where there was any suspicion that interference or matrix effect was present.

  - All samples containing a measurable concentration of analyte.
  - In addition, at least one sample in every seven.

b. The level of spike chosen was controlled by the following factors:

  - It should approximately double the apparent concentration.
  - If this results in an absorbance greater than that of the highest standard, the spiked sample is suitably diluted with distilled water.

c. A reagent blank was run with each set of spiked samples prepared.

During the sampling program*, the standard protocol followed for metals analysis was:

1. Ten of the 13 toxic metals were determined by AA spectrophotometry in the furnace mode, namely Ag, Be, Cd, Cu, Cr, Ni, Pb, Tl, Sb and Zn.

2. If matrix interference were seen, samples were spiked and redetermined.

3. If difficulties due to excessively high detection limits were found for the four elements Cd, Pb, Sb and Tl, the determination was repeated in the furnace (HGA) mode for these four elements.

4. Selenium and arsenic were determined by hydride generation using sodium borohydride ($NaBH_4$).

5. Mercury was determined by the standard cold vapor method.

*During the Phase I program, excessive interferences with metals analyses were encountered in some subcategories which were solved by changing the AA methods to the flame mode. During Phase II, the flame mode was used as the first step (because of the experience in Phase I), but when excessively high detection limits were found, the furnace mode was used to allow determination with lower detection limits.

Table 5-1 presents the analytical detection limits of the various methods for the 13 toxic metals.

TABLE 5-1. ANALYTICAL DETECTION LIMITS FOR TOXIC METALS(1)

	Method Detection Limit (ug/l)(2)			
Element	Flame Method	Furnace Method (HGA)*	Gaseous Hydride Method	Cold Vapor Method
Antimony, Sb	200	3		
Arsenic, As			1	
Beryllium, Be	5	0.2		
Cadmium, Cd	5	0.1		
Copper, Cu	20	1		
Chromium, Cr	50	1		
Lead, Pb	100	1		
Mercury, Hg				0.2
Nickel, Ni	40	1		
Selenium, Se			2	
Silver, Ag	10	0.2		
Thallium, Tl	100	1		
Zinc, Zn	5	0.05		

* Heated Graphite Atomizer

(1) Assuming no matrix interferences requiring dilution of sample.

(2) "Methods for Chemical Analysis of Wastes and Water," USEPA Environmental Monitoring and Support Laboratory office of Research and Devlopment, Cincinnati, OH (March 1979). This Manual has been revised periodically to incorporate slight changes in methods and to add alternate methods. Methods used in Phase II are the same as have been used previously in Phase I, and the data are directly comparable.

B. Organic Compound Analysis

The organic toxic pollutants were determined by the standard protocol (40 CFR 136 proposed December 3, 1979, 44 FR 69464) which includes sample preparation, extraction, and analytical methodologies (Methods 624 and 625, "superscreened"). "Superscreening" is the term utilized by the Agency to denote a series of procedures which were utilized for organic parameter analyses during Phase II. In these procedures, one sample from each sampling episode (for each site) was split and analyzed in duplicate to provide information on the precision of the method(s) being employed. At one site, for one day, replicate samples were taken for recovery information (may be same site at which precision sample was obtained). The same pattern was followed for VOA samples for quality assurance/quality control. During the Phase II program, organic analyses were performed at each sample site on one day (usually the second day).

Extractions were carried out using methylene chloride in the case of the acid and base/neutral organic fractions and with hexane/methylene chloride to obtain the pesticide-containing fractions. The acid and base/neutral fractions were reduced in volume and analyzed by gas chromatography-mass spectrometry (GC/MS). The pesticides were analyzed by electron capture gas chromatography followed by GC/MS confirmation of positive results. Volatile organics were analyzed by the purge and trap method of introducing the material into the GC/MS inlet system.

C. Cyanide Analysis

The standard methods for the wet chemical analysis of total cyanide and cyanide amenable to chlorination (Cyanide A) were utilized (40 CFR 136). Cyanide analysis is subject to several sources of interference including:

1. Metals - The presence of Fe, Cd, Ca, Ni, Ag, and Zn may cause measurement errors on the low side due to the formation of stable complexes with cyanide. The iron complexes may form insoluble precipitates which are particularly difficult to break up both at the time of treatment (alkaline chlorination) of the sampled wastewater and during the chemical analysis for cyanide.

2. Oxidizing agents - The presence of free chlorine in the wastewater sample will destroy cyanide and cause

measurement errors on the low side. The addition of ascorbic acid to destroy chlorine at the time of sampling is intended to mitigate this problem. Other oxidizing agents such as peroxides and chromates may also react with cyanides over a period of time and cause low results.

3. Sulfides - Sulfide or bisulfide will interfere in the analysis of cyanide by reacting with the colorimetric reagents.

The presence of sulfur dioxide or bisulfite in the wastewater sample should have no appreciable effect on cyanide results. Detection limits on the order of 1-4 μg/l can be achieved by the analytical method employed, but the results have to be interpreted with regard to the possible interfering components of the sample.

D. Asbestos Fiber Analysis

The analysis of selected samples for asbestos fiber (chrysotile) was conducted by the recommended method utilizing transmission electron microscopy with selected area electron diffraction as described by Dr. Charles Anderson (EPA, Athens, Georgia) at the Analytical Protocol Meeting in Denver (November 1977) (2).

E. Conventional and Nonconventional Pollutants

All techniques used for the analysis of conventional and nonconventional pollutants were those recommended by the Agency. The list of approved test procedures was published in the Federal Register on October 16, 1973 (38 FR 28758) and amended December 1, 1976 (41 FR 52780) and may be also found in Title 40 of the Code of Federal Regulations (40 CFR 136).

Quality Assurance Provisions

The Agency and the contractor's analytical laboratories maintain consistently high standards for accuracy and quality control. As an in-house requirement, a minimum of ten percent of all samples are routinely run in duplicate. Quantification is based on standards which are prepared in pure water, at concentrations such that all sample measurements are greater than the absorbance of the lowest standard, and less than the absorbance of the highest standard. The standards are also checked by participation in the EPA Reference Sample Program that utilizes a double blind technique. (EMSL, Cincinnati, Ohio, Office of Research and Development.)

Additionally, outside laboratories are retained for checks on quality by analyzing split samples and running submitted standards. Accuracy is also insured by analysis of a minimum of fifteen percent of all samples with spikes by the method of standard additions. The spikes are added prior to sample preparation and are carried through the entire sample analysis procedure.

The contractor's laboratories have consistently maintained the standards for laboratory certification which are imposed by the State of California. Certification is dependent upon the accurate performance of routine analyses on check samples submitted by the State, as well as on-site inspections by the State of California's Sanitation and Radiation Laboratory, Department of Fish and Game, and the U. S. Environmental Protection Agency, NEIC, Denver, Colorado.

The quality assurance provisions outlined in the EPA Protocol for GC/MS Analysis of Toxic Pollutants are rigorously adhered to with one added precaution, namely, the use of internal standards as a means of measuring recovery. Although not required by the protocol for pesticide analysis, this technique is utilized as an in-house quality control requirement to ensure the accuracy of results in this analysis.

The high sensitivity of instrumentation used in trace organic chemical analysis dictates that contamination of the samples from any possible source must be diligently guarded against. Accordingly, only glass sample containers with Teflon-lined lids were used and these were subjected to a three step cleaning procedure prior to use, even though only new liners and glass containers were used. All glassware used for sample preparation and analysis was subjected to a dual cleaning system.

The sample extraction and preparation rooms are dedicated solely to toxic pollutant analysis, and have their own ventilation systems that are isolated from the other sample preparation and receipt areas of the laboratories.

A documented system of existing practices, including calibrations and operational checks is maintained to assure uniformity of performance and to serve as a basis for alteration of standardization intervals. A chemist is assigned full time to maintain this system, assure strict record formatting and controls, and to direct the quality control program of the laboratories. The primary vehicle of this system is the quality assurance manual containing the detailed procedures used in sample preparation and analysis, and the complete records of all quality control standards, blanks, spikes and duplicates.

SUMMARY OF ANALYTICAL RESULTS

There are 46 plants producing the 17 chemical products listed in the six proposed subcategories. Many plants produce several products listed under the Phase II program as well as products also covered under Phase I previously. Thirteen plants were visited during the sampling program for this study. One plant was sampled twice.

The results obtained during the sampling program are summarized in Table 5-2 and 5-3. These tables show the frequency and distribution of the pollutants according to selected plant groupings, concentration ranges, and subcategories in which the pollutants occur.

Pollutant frequencies are based upon the highest individual pollutant concentration found for each plant's raw and treated wastewater during the sampling program.

The toxic pollutant asbestos has not been included in either of the tables mentioned above. Asbestos concentrations for those sites sampled for asbestos are reported in Table 5-4. All values are expressed as million fibers per liter (MFL) or mass per unit volume.

The treated effluent concentration of asbestiform fibers observed in this industry group is considered to be low and close to the limits of detection of the methods employed.

TABLE 5-2. POLLUTANT FREQUENCY BASED ON SAMPLING
RESULTS (RAW AND TREATED WASTEWATER)*

		Pollutant Occurrence Based on Concentration (ug/1)			
	Priority Organics Detected**	≤ 50	≥ 50 but ≤ 500	≥ 500 but ≤ 2500	≤ 2500
1B	acenaphthene	4			
3V	acrylonitrile	2			
4V	benzene	17	2		
6V	carbon tetrachloride	6	3		
7V	chlorobenzene	6			
10V	1,2-dichloroethane	1		2	4
11V	1,1,1-trichloroethane	4			
12B	hexachloroethane	1			
13V	1,1-dichloroethane	8			
14V	1,1,2-trichloroethane	6			
16V	chloroethane	5			
18B	bis(2-chloroethyl)ether		2		
21A	2,4,6-trichlorophenol	3			
23V	chloroform	43	9	1	1
24A	2-chlorophenol	1			
27B	1,4-dichlorobenzene	1			
29V	1,1-dichloroethylene	7			
30V	1,2-trans-dichloroethylene	5			
31A	2,4-dichlorophenol	2			
32V	1,2-dichloropropane	3			
37B	1,2-diphenylhydrazine	2			
39B	fluoranthene	1			
44V	methylene chloride	45	2		5
45V	methyl chloride	5	2	3	
47V	bromoform	4	1		
48V	dichlorobromomethane	21			
49V	trichlorofluoromethane	6	1		
51V	chlorodibromomethane	16			
54B	isophorone	2			
56B	nitrobenzene	1			
58A	4-nitrophenol	1			
59A	2,4-dinitrophenol	1			
60A	4,6-dinitro-o-cresol	1			
62B	n-nitrosodiphenylamine	1			
64A	pentachlorophenol	4			
65A	phenol	7			
66B	bis(2-ethylhexyl) phthalate	37	1		
67B	butyl benzyl phthalate	7			
68B	di-n-butyl phthalate	31			

TABLE 5-2 (continued)

Priority Organics Detected		Pollutant Occurrence Based on Concentration (ug/l) ≤50	>50 but ≤500	>500 but ≤2500	≤ 2500
69B	di-n-octyl phthalate	14			
70B	diethyl phthalate	17			
71B	dimethyl phthalate	2			
72B	benzo(a)anthracene	4			
76B	chrysene	5			
81B	phenanthrene	1			
85V	tetrachloroethylene	12			
86V	toluene	18			
87V	trichloroethylene	7			
88V	vinyl chloride	5			
89P	aldrin	9			
90P	dieldrin	10			
91P	chlordane	1			
92P	4,4' -DDT	2			
93P	4,4' -DDE	9			
94P	4,4' -DDD	10			
95P	α-endosulfan	3			
96P	β-endosulfan	4			
97P	endosulfan sulfate	3			
98P	endrin	4			
100P	heptachlor	8			
101P	heptachlor epoxide	3			
102P	α-BHC	27			
103P	β-BHC	4			
104P	γ-BHC	14			
105P	δ-BHC	30			

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*Blank spaces in this table denote concentration levels which did not occur in the wastewater samples analyzed.

**A = Acid fraction
B = Base/Neutral fraction
V = Volatile fraction
P = Pesticide fraction

TABLE 5-3. PRIORITY ORGANICS DETECTED BY SUBCATEGORY (RAW AND TREATED WASTEWATER; ≥ 10 ug/l)

Priority Organics Detected		Subcategory
3V	acrylonitrile	5
4V	benzene	5
6V	carbon tetrachloride	5, 6
10V	1,2-dichloroethane	5
12B	hexachloroethane	5
16V	chloroethane	5
18B	bis(2-chloroethyl)ether	1
21A	2,4,6-trichlorophenol	3, 5
23V	chloroform	1, 3, 4, 5
31A	2,4-dichlorophenol	5
37B	1,2-diphenylhydrazine	3
44V	methylene chloride	1, 3, 4, 5, 6
45V	methyl chloride	5
47V	bromoform	3
48V	dichlorobromomethane	3, 5
49V	trichlorofluoromethane	5
51V	chlorodibromomethane	3
54B	isophorone	1
58A	4-nitrophenol	1
59A	2,4-dinitrophenol	1
60A	4,6,-dinitro-o-cresol	1
64A	pentachlorophenol	1
65A	phenol	5
66B	bis(2-ethylhexyl) phthalate	1, 3
68B	di-n-butyl phthalate	1
69B	di-n-octyl phthalate	5
85V	tetrachloroethylene	3
86V	toluene	3
88V	vinyl chloride	5
103P	β-BHC	3

Subcategory

1 = Cadmium Pigments and Salts
2 = Cobalt Salts
3 = Copper Salts
4 = Nickel Salts
5 = Sodium Chlorate
6 = Zinc Chloride

TABLE 5-4. OCCURRENCE OF ASBESTIFORM FIBERS BY PLANT

Plant	Influent/ Effluent	Total Fibers (MFL)	Chrysotile Fibers (MFL)	Detection Limit (MFL)	Total Calculated Mass (Chrysotile only) ug/l
F122	E	85	20	0.8	0.3
F102	I	283	170	56.7	4.51
F102	E	<7	<7	7	---
F107	E(1)	1630	15	15	0.3
F107 (Shaken)	E	1100	890	12	5.4
F107 (Settled)	E	840	252	12	2.7
F134	I	186	<6	6	---
F134	I	7.2	<1.2	1.2	---
F134	E	<3	<3	3	---
F134	E	16.2	1.2	0.6	0.017
F117	I	0.96	<0.12	0.12	---
F117	E(2)	12	<1.2	1.2	---
F117	E(2)	5.4	<0.3	0.3	---

I = influent
E = effluent
MFL = million fibers per liter

(1) Untreated
(2) Two different waste streams

SECTION 5

REFERENCES

1. Sampling Screening Procedure for the Measurement of Priority Pollutants, U.S. Environmental Protection Agency, 1976, 6pp.

2. Anderson, C. H. and Long, J. M. Interim Method for Determining Asbestos in Water. EPA-600/4-80-005, U.S. Environmental Protection Agency, Athens, Ga., 1980.

SECTION 6

PROCESS AND WASTEWATER TREATMENT INFORMATION DEVELOPMENT AND EVALUATION

INDUSTRY DATA BASE DESCRIPTION

Information and data on the inorganic chemicals industry were obtained from a number of sources. These sources included literature reviews, plant visits, telephone contacts, lead visit reports, industry responses to the Agency's request for data under Section 308 of the Act (the "Section 308-Questionnaires"), visits by EPA personnel, self-monitoring (NPDES) reports and additional data supplied by industry after publication of the proposed regulation. The type of material gathered from these sources is discussed below.

Literature Review

A review of the literature was conducted to identify and collect information related to manufacturing processes, raw materials, water use, wastewater sources, wastewater treatment technology, raw waste characteristics, and economic data. Relevant information from reports, books, papers, conference presentations and periodicals were identified by computer search and are presented in the reference section of this report. This information was incorporated into a broad-based assessment of process and technology practices aimed at selecting the best available treatment technology and best demonstrated technology for the various industry subcategories. It also provided the background required for evaluating the proposed subcategorization of the chemical products.

Plant Visits

During the screening and verification phase of this project, much information was gathered from individual plants relating to production capacity, manufacturing processes, waste flows, water reuse, wastewater treatment systems and performance, and best management practices (BMP). In October and November 1982, EPA personnel visited 12 plants to update and clarify some of the information given in the Section 308-Questionnaires. Nine of the twelve had not been visited previously in this study.

Telephone and Direct Contact

Numerous contacts were made with knowledgeable persons in both industry and government to gather and exchange information concerning all phases of this study. These sources are cited in the text as personal communications.

308-Questionnaire Responses

The basis for much of the work in this study is the responses from industrial inorganic chemical firms to the Section 308 data requests.

Data from all of the 46 plants were utilized by the project team for the development of appropriate guidelines for the inorganic chemicals subcategory. Industrial firms, through their compliance with the needs of the Section 308-Questionnaire, provided a valuable industry-wide data base used extensively in this analysis.

Essential data elements from the questionnaires were used for the purpose of creating a working data base for this report. The types of information obtained for the data base are presented in Table 6-1.

These data provided the basis for the subcategory review through a profile of each industry. After compilation of the questionnaire data, industry totals for capacity and production (for the respondents) were available. In addition, derivative quantities such as percent utilization, effluent per ton of product, and conversion to metric units were compiled.

Treatability Study

Beside the treatability study conducted during Phase I, a treatability study was conducted during Phase II at one zinc chloride facility(1). The purposes of this study were to evaluate the effectiveness of granular media filter technology, to establish a relationship between total and dissolved zinc in the treated process water effluent, and to determine the treatment levels attained by filtration technology for TSS, total zinc, total lead, and total arsenic. This study was conducted in April 1984 and is described in more detail in Section 16.

New Data

Public comments on the proposed regulation were a significant source of new data. Industry commenters supplied extensive new long-term data on treatment efficiency in the cadmium pigments and salts industry, providing both influent and effluent data for our evaluation. In addition, one EPA Regional office provided a compliance monitoring and inspection report for a zinc chloride plant which greatly assisted our understanding of the treatment process and efficiency at that plant.

PROCESS WASTEWATER SOURCES AND CURRENT TREATMENT PRACTICES

Data Acquisition

The information presented in this section was obtained from a variety of published sources and the available industry responses to the 308-Questionnaires as well as from plant visits and interviews with industry personnel conducted by the Agency and its contractors during the toxic pollutant screening and verification program. The results of visits and interviews were documented in field notebooks for the preparation of interim plant visit reports and telephone communication records which are both part of the rulemaking record.

Plant visits were particularly useful for obtaining the detailed technical information necessary for creation of the data base. The cooperative attitude displayed by industry greatly facilitated the acquisition of reliable operating data and meaningful sampling results.

Evaluation of Data

Each of the various industrial subcategories in which sampling was conducted was the subject of an extensive evaluation to provide the technical basis for selecting candidate advanced treatment technologies and developing the related base and incremental cost estimations.

TABLE 6-1. 308 QUESTIONNAIRE RESPONSE DATA ELEMENTS

INORGANIC CHEMICALS GUIDELINES STUDY

Datum Reference	Description	Comments
Manufacturer	Name Location EPA Region	Confidential
Product	Name	
	Subcategory	Inorganic Chemicals
	Number of other Products	
Plant	Capacity	Primarily FY 1980
	Production Age	
Process	Name Volume of Process Effluent Volume of Noncontact Effluent	Operating Days
Effluent Treatment	Type Permit Number, or POTW District Major Pollutants Long-term Treatment Results	
Costs	Wastewater Treatment Facilities and Equipment Treatment Reagents Energy Solid and Hazardous Waste Disposal	

Individual plant descriptions are presented later in this report according to the following general format for each subcategory:

General Process Description
  Description of process reactions and unit operations.
  Inventory of raw materials used.
  Typical process flow diagram.

- Water Use and Waste Source Inventory
  - Description of individual plants visited, sampled and plant information from other sources.
  - Inventory of water uses for contact and noncontact purposes.
  - Inventory of raw process wastewater sources and identification of sampling points.
  - Process wastewater quality and flow data.
  - Solid waste generation and disposal.

- Control and Treatment Practices
  - Description of specific treatment technologies and operating facilities.
  - Description of the total input to the treatment system including sources attributed to other production operations and noncontact water (e.g., cooling water).

- Evaluation of Production and Wastewater Flow Data
  - Tabular summary of plant-specific data.
  - Waste flows per unit of production (unit wastewater flows) with the range and average values.
  - Solid waste quantities generated by treatment.
  - Treatment chemical requirements.

- Process Modifications and Technology Transfer Options

- Best Management Practices (BMP)
  - Plant area operations and housekeeping.
  - Runoff control.
  - Solid waste handling (e.g., fugitive dust and leachate control, etc.).

Model Plant and BPT Treatment System Specification

The model plant concept plays a central role in both the development of alternative treatment system designs for priority pollutant removal and for estimating the related internal costs of such treatment in each subcategory. In order to be representative of a subcategory, each set of model plant specifications was composited from a profile data summary derived from the available information on production and wastewater flow.

Based on typical wastewater flow and production, the model plant was used as a starting point for an appropriately designed and sized wastewater treatment system. Certain assumptions were made regarding the possible process variations and the specific raw wastewater sources incorporated into each model. In most cases, it was necessary to assume that the wastewater flow per unit of production did not vary over the particular range of production capacities covered. (There was little variation in flow from plants that provided reliable data.) Production rates were selected in most subcategories to represent a range in sizes of plants presently in operation. Small subcategories were represented by single mid-range production rates for the model plants. Cost estimates were developed for each set of treatment system design specifications.

Beginning with Section 11, the model plant and treatment system descriptions for each level and specifications for each subcategory include the following information:

1. Production rates and mode of operation
2. Specific process type and wastewater sources
3. Wastewater flow per unit of production
4. Solid waste generation and handling
5. Treatment reagent requirements

The model plants do not represent exemplary or specific existing plants, but are typical plants of adequate design derived from the range of plants, treatment facilities, and production characteristics found in the entire subcategory. For the purpose of cost estimating, it is necessary to specify cost rationale, define a set of initial assumptions, and consider the variability of factors such as wastewater flows, pollutant concentrations, unit treatment process, plant age, etc. General assumptions have been detailed under Section 10 of this report and are employed as the basis for developing baseline model plant cost estimates presented in the subsequent sections dealing with individual industries. The use of model plant cost estimates to assess the economic impact of compliance costs for real plants is not always accurate, particularly with respect to plants with wastewater flows varying greatly from the model plant. Accordingly, we have used plant-specific data to estimate compliance costs for the cobalt salts, copper salts, nickel salts, and zinc chloride subcategories, and the cadmium salts segment of the cadmium pigments and salts subcategory. Most plants in those subcategories are multi-product plants. The plant-specific compliance cost estimates were used to assess the economic impact of the regulation.

Dissolved Solids in Wastewater Effluent

Many wastewater treatment plants discharge final effluent into watercourses which feed fresh water streams used as sources of water supply by downstream agencies or industries. Groundwater aquifers which underlie large portions of the country are tapped to supply fresh water through wells serving public and industrial water needs. Saline wastes discharged into streams or into unlined lagoons can significantly alter the total dissolved solids content of the fresh water. Although Federal regulations seldom limit the total dissolved solids or the various ions such as chloride, sulfate, bicarbonate, and nitrate, these constituents can be of serious concern to local water users.

To protect the mineral quality of ground and surface waters, state and local water pollution control agencies typically establish limits on the discharge of substances which contribute sodium, potassium, hardness, chloride, sulfate, or conductivity, which is a measure of total solids in solution. This restriction can affect the chemicals chosen for wastewater treatment. For example, alkaline precipitation can be accomplished by using lime, which forms an insoluble calcium sludge, or by adding caustic soda, forming a soluble sodium salt.

In choosing an acid for neutralization of alkaline wastes, it is important to weigh the overall effects of chloride (from hydrochloric acid) and sulfate (from sulfuric acid), particularly with respect to irrigational use of the receiving water.

Chemicals used in the model plant processes were selected on the basis of best performance, including consideration of scaling problems, which can be severe when calcium and sulfate are at saturation levels. It may be necessary to alter the nature of chemicals used at a specific plant, in order to meet local water quality requirements.

SECTION 6

REFERENCES

1. Harty, D.M., Funke, D.M., and Terlecky, P.M., "Dual-Media Filtration Treatability Test Results at Zinc chloride Plant F144," Frontier Technical Associates, Inc. Report No. FTA-84-E6-01, June 27, 1984.

SECTION 7

ASSESSMENT OF TECHNOLOGY FOR ADVANCED TREATMENT AND CONTROL

INTRODUCTION

In the inorganic chemicals industry, pollution abatement practices vary and a wide range of treatment technologies can be found, ranging from no treatment to the application of highly advanced technologies for the removal of specific pollutants.

Until the NRDC Settlement Agreement, industry attention was primarily directed toward general pollution problems including removal of trace metals, but not toward treatment of over 100 individual specific organic compounds now listed as toxic pollutants. Even with the classical (conventional and nonconventional) pollutants, treatment technology had been directed to removal down to the part per million level, whereas now the thrust is toward part per billion level requirements. For both of these reasons, higher level technologies are sometimes not in place in the inorganic chemicals industry, and therefore it is necessary to examine technologies that have been applied in other industries or developed at the laboratory or pilot-plant scale specifically for the removal of these toxic substances from industrial wastewater, and determine whether they can be adopted as viable technological options.

A list of candidate technologies was compiled from the literature, in-house expertise, and industry contacts. These were evaluated with respect to:

1. Treatment effectiveness
2. Cost
3. Nonwater pollution environmental effects
4. Applications in the inorganic chemicals industry or on other industrial wastes with similar wastewater characteristics.

The anticipation that few of the organic toxic pollutants would be found in inorganic chemical wastes in treatable concentrations was justified by the results of the analytical programs in both Phase I and II. As a result, the initial search for candidate BAT technologies became limited to treatment technologies for the thirteen metals.

The technologies finally adopted were not new or untried technologies since it was found that most treatment requirements could be met by taking conventional techniques--for example, chemical precipitation--and developing them to a higher degree of engineering and design sophistication, so that optimum removal efficiencies could be achieved.

The following pages describe the theoretical basis for treatment systems considered for application in this group of subcategories.

HYDROXIDE PRECIPITATION

Hydroxide precipitation is the most widely used technology for removing trace metals from wastewaters, with lime or caustic soda commonly used to supply the hydroxide ions. Under suitable conditions the metals form insoluble metal hydroxides which can be separated from solution.

The chemistry of the process is not simple, and must be understood for each metal. Many metals are amphoteric, the optimum pH for precipitation varies, and organic complexes can interfere. A simple form of the reaction may be written as:

$$M^{++} + 2OH^- = M(OH)_2 \qquad (1)$$

Metal ion + two hydroxyl ions = insoluble metal hydroxide

If the pH is below the optimum for hydroxide precipitation soluble complexes form:

$$M^{++} + OH^- = M(OH)^+ \qquad (2)$$

Metal ion + hydroxyl ion = soluble metal complex

Since most metals have the capability of coordinating with other ions or molecules, these simple equations assume that the hydroxyl ion is the coordinated species. However, if organic radicals are present, they can form chelates and mask the typical precipitation reactions:

$$M^{++} + OH^- + nR = M(R)n(OH)^+ \qquad (3)$$

Metal ion + hydroxyl ion = soluble metal
+ organic ions chelate

Such complexes may require unusual treatment to hydrolyze them, and their presence often explains why some treatment practices yield relatively poor results.

TABLE 7-1. SOLUBILITY PRODUCTS OF TOXIC METALS

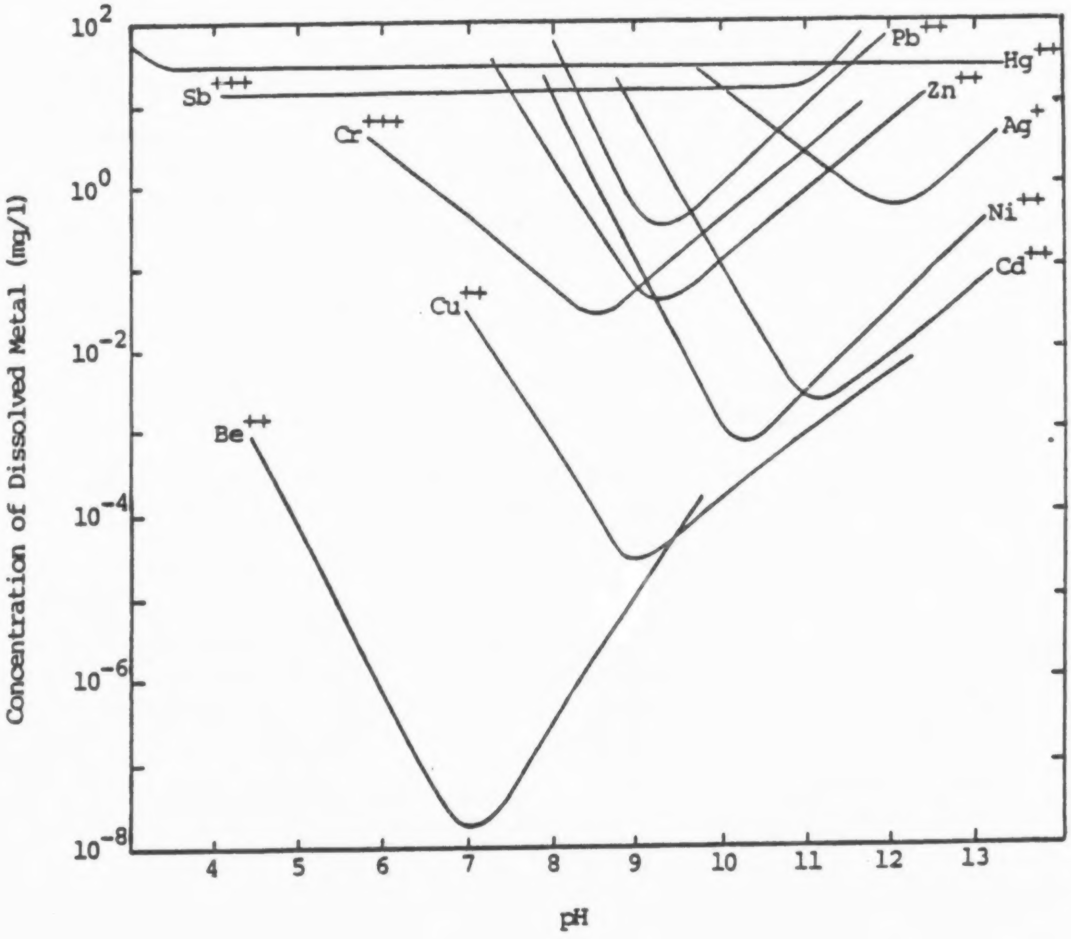
Metal	Solubility Product Constant (K_{sp}) Metal Hydroxide	Solubility Product Constant (K_{sp}) Metal Sulfide
Antimony (III)	--	—
Arsenic	--	—
Beryllium	1.6×10^{-22} (1)	—
Cadmium	2.5×10^{-14} (1)	3.6×10^{-29} (2)
Chromium (III)	6.3×10^{-31} (1)	—
Copper	2.2×10^{-20} (1)	8.5×10^{-45} (2)
Lead	1.2×10^{-15} (1)	3.4×10^{-28} (2)
Mercury	3.0×10^{-26} (1)	2.0×10^{-49} (2)
Nickel	2.0×10^{-15} (1)	1.4×10^{-24} (2)
Selenium	—	—
Silver	2.0×10^{-8} (1)	1.6×10^{-49} (2)
Thallium (I)	—	5.0×10^{-21} (1)
Zinc	1.2×10^{-17} (1)	1.2×10^{-28} (2)

NOTE: References for above values are shown below.

(1) Dean, J.A., Ed., Lange's Handbook of Chemistry, 12th ed., McGraw-Hill Book Co., New York, 1979.

(2) Weast, R.C., Ed., Handbook of Chemistry and Physics, 57th ed., CRC Press, Cleveland, Ohio, 1976.

Figure 7-1. Theoretical solubilities of toxic metal hydroxides/oxides as a function of pH.



NOTE: Solubilities of metal hydroxides/oxides are from data by M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, Oxford, 1966.

Assuming the absence of organic complexing agents, the treatment levels attainable by hydroxide precipitation can be forecast from a knowledge of the pH of the system. Figure 7-1 shows the theoretical solubility of those toxic metals which form insoluble hydroxides, while Table 7-1 shows the solubility product constants. For comparison, the values for sulfides are also given in Table 7-1.

It is clear from the range of optimum pH's illustrated that for wastewaters containing more than one metal, no single optimum pH exists, and problems arise at the threshold of the alkaline range (circa pH 10) where some metals have least solubility, while others are at the point of redissolving as an anionic species. For successful application as a wastewater treatment technology, careful control of pH must be practiced if the best removals are to be achieved.

In practice the solubility of metallic hydroxides, and the tendency for fine insolubles to remain in suspension, may yield effluents which will not meet µg/l standards, and hydroxide precipitation is often supplemented by the use of coagulating agents or filtration to improve solids removal.

In practice, the technology uses unit process steps which are simple, well-established, and well-understood by the industry.

Depending on the quantity of waste flow, the treatment can either be a batch or continuous operation, with batch treatment being favored when wastewater flows are small. In batch treatment the equipment usually consists of two tanks, each with a capacity to treat the total wastewater volume expected during the treatment period. These systems can be economically designed for flows up to 50,000 gallons per day (1).

The treatment tanks serve the multiple functions of equalizing the flow, acting as a reactor and as a settler. During operation the wastewater is stirred, and a homogeneous sample is taken and analyzed to determine the chemical dosage requirements. The chemicals are then added, mixed and stirred for about 10 minutes. After the reaction is complete, the solids are allowed to settle for a few hours. The clear liquid is then decanted and discharged. Settled sludge is retained to serve as a seed for crystal growth for the next batch, but must be drawn off periodically and disposed of, usually in a chemical landfill.

For larger daily flows, a typical continuous flow treatment scheme consists of a flash mixing tank and reagent feed system, settling unit with sludge storage and disposal and, in some cases, final pH adjustment and/or a filtration system.

The ability to separate the solids from the wastewater is important. Metallic hydroxides tend to be gelatinous and separate poorly in gravity separators. Finely suspended solids tend to pass out with the effluent and increase the total metal content. Thus, improvements in precipitation applications have been directed toward fine solids removal, and this is reflected in the addition of various filtration systems and the use of flocculant aids as improved levels of treatment.

Soda ash (sodium carbonate, Na_2CO_3) is sometimes found to be the reagent of choice particularly for lead removal. Lead carbonate, $PbCO_3$, and lead hydroxide/carbonate, $2PbCO_3 \cdot Pb(OH)_2$, (basic carbonate) are formed which may afford improved settling properties for a particular waste.

Hydrated lime suspensions are more commonly used than soda ash or caustic soda as the hydroxide source because they are more economical. However, if there is sulfate ion present in the waste water, gypsum will be formed:

$$Ca(OH)_2 + (SO_4)^{--} = CaSO_4 + 2OH^- \qquad (4)$$

Hydrated lime + sulfate ion = calcium sulfate (gypsum) + hydroxyl ions

This increases the sludge produced, may cause scaling problems in pipelines, and may clog a granular media filter. Using caustic soda is more expensive, but it generally eliminates the scaling problem. Total dissolved solids in the form of sodium salts are increased in the caustic soda treated wastewater. Although low concentrations of sodium are not regarded as polluting, high levels can make drinking water unpalatable, limit the use of water for agriculture, and promote degradation of the structure of arable soils. Thus, where high total dissolved solids are of concern, lime would be the preferred neutralizing agent.

This treatment technology is widely applied in treating industrial wastewaters that contain metals. Industries that are using hydroxide precipitation to remove metals from wastewater include:

- Inorganic Chemicals,
- Plating and Metal Finishing,
- Ore Mining and Dressing,
- Textiles,
- Iron and Steel,
- Non-Ferrous Metal Processing,
- Electronics,
- Copper Forming,

- Coal Mining

Better than 99 percent removal of trace metals have been reported in the literature with final concentrations in the treated effluents ranging from sub ppm to low ppm (see Tables 8-1 through 8-10). The data also show that the concentrations and solubility products are the determining factors in evaluating candidate technologies. Therefore, it is appropriate to transfer this technology to industries not currently using this technology if the wastewater contains metals.

FERRITE COPRECIPITATION

An interesting variation on the theme of hydroxide precipitation is a process developed in Japan for the removal of heavy metals from acidic wastewater. The process, known as ferrite coprecipitation, has the potential for producing a marketable residual by converting the metal ions in solution into insoluble ferromagnetic oxides or ferrites which can be removed magnetically or by filtration (1). The treatment is applied by adding a ferrous salt to the metal-bearing wastewater, then neutralizing and oxidizing the complex heavy metal-ferrous hydroxide precipitate by aeration to form the stable ferrite coprecipitate. Particle sizes are reported to be relatively large and sludges formed can be safely disposed of by landfilling.

Although extensive performance data have not been developed, the information available indicates that very high removal efficiencies can be achieved for most of the common heavy metals, including mercury and hexavalent chromium. The method has not been considered here as an available technology due to the lack of sufficient information on chemical dosage requirements, energy requirements, and performance in situations similar to those found in the inorganic chemicals industry.

SULFIDE PRECIPITATION

The basic principle of sulfide treatment technology is similar to that of hydroxide precipitation. Sulfide is added to precipitate the metals as metal sulfides, and the precipitate formed is separated from the solution by gravity settling or filtration. Sodium sulfide and sodium bisulfide are the two chemicals commonly used, with the choice between these two precipitation agents being strictly an economic consideration.

Metal sulfides form according to the following equation:

$$M^{++} + Na_2S = MS + 2Na^+ \qquad (5)$$

Metal ion + sodium sulfide = insoluble metal sulfide
+ sodium ions

In order to calculate the theoretical solubilities of the metal sulfides as a function of pH, the equilibria involved in solid metal sulfide dissociation are taken into account:

$$MS = M^{++} + S^{--} \qquad (6)$$

Metal sulfide = metal ion + sulfide ion and, depending on pH, the sulfide ion can react with hydrogen ions to form the bisulfide ion and hydrogen sulfide.

$$S^{--} + H^{+} = HS^{-} \qquad (7)$$

Sulfide ion + hydrogen ion = bisulfide ion

$$HS^{-} + H^{+} = H_2S \qquad (8)$$

Bisulfide ion + hydrogen ion = hydrogen sulfide

The concentration of metal ion in solution will equal the concentration of sulfide ion, bisulfide ion and hydrogen sulfide. Knowing the metal sulfide solubility product (Table 7-1) and the acid dissociation constants of hydrogen sulfide, $K_1 = 9.1 \times 10^{-8}$, $k_2 = 1.1 \times 10^{-12}$ (see Reference 2 in Table 7-1) the solubility of the metal ion can be calculated as a function of the hydrogen ion concentration and, therefore, as a function of pH.

For a divalent metal ion the equation is:

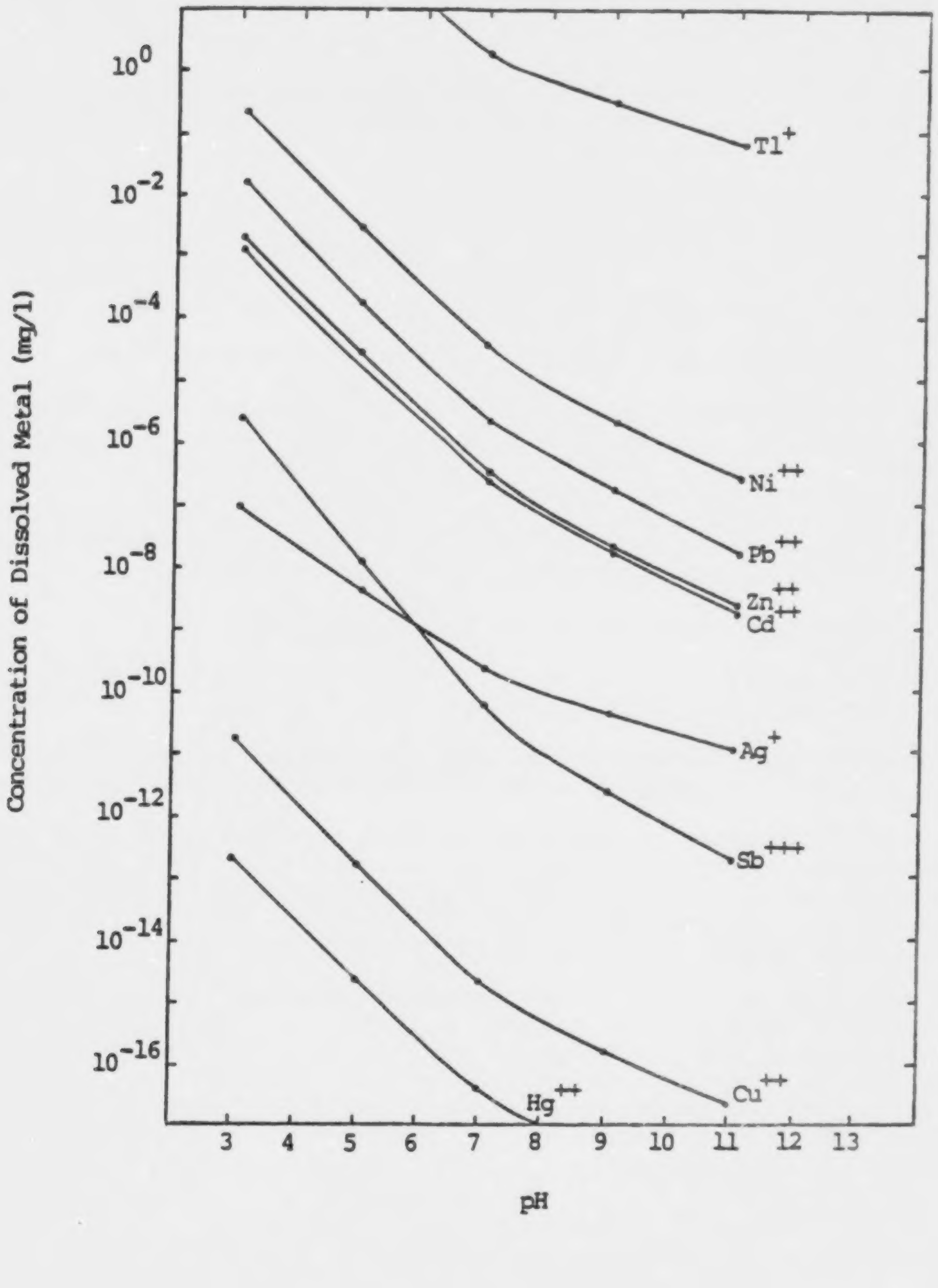
$$(M^{++}) = [Ksp\ [1 + (H^{+})/(1.1 \times 10^{-12})] + (H^{+})^{2}/(1 \times 10^{-19})]^{\frac{1}{2}}$$

Using the above information, the theoretical solubilities of the toxic metal sulfides were calculated and are shown in Figure 7-2.

The major problem in applying sulfide precipitation techniques is associated with the toxicity of sulfides. This warrants both care in application and post treatment systems to remove excess sulfide. Pretreatment involves raising the pH of the waste stream to minimize evolution of hydrogen sulfide gas.

A recently developed and patented process to eliminate the potential hazard of excess sulfide in the effluent and the formation of gaseous hydrogen sulfide uses ferrous sulfide as the sulfide source (2). The fresh ferrous sulfide is prepared by adding sodium sulfide to ferrous sulfate. The ferrous sulfide slurry formed is added to a wastewater to supply sufficient

Figure 7-2. Theoretical solubilities of toxic metal sulfides as a function of pH.



sulfide ions to precipitate metal sulfides which have lower solubilities than ferrous sulfide. Typical reactions are:

$$FeS + Cu^{++} = CuS + Fe^{++} \qquad (10)$$

Ferrous sulfide + copper ion = insoluble copper sulfide + iron ion

$$FeS + Ni(OH)_2 = Fe(OH)_2 + NiS \qquad (11)$$

Ferrous sulfide + nickel hydroxide = ferrous hydroxide + insoluble nickel sulfide

A detention time of 10-15 minutes is sufficient to allow the reaction to go to completion (3). Ferrous sulfide itself is also a relatively insoluble compound. Thus the sulfide ion concentration is limited by the solubility of ferrous sulfide, which amounts to about 0.02 mg/l, and the inherent problems associated with conventional sulfide precipitation are minimized (4).

One other advantage of this process is that if chromium (VI) is present, it will also be reduced at the pH of normal operation (8 to 9) and precipitate as the trivalent hydroxide (Cr III).

Treatment systems for sulfide precipitation are similar to those used for hydroxide precipitation. A continuous treatment scheme generally consists of a pH adjustment tank and reagent feed system, settling unit, ferrous sulfide addition system, flash mixing tank, granular media filter, and sludge storage and disposal.

Before the addition of sodium sulfide or bisulfide the pH of the incoming wasteflow is adjusted to pH of 7-8 in the first reaction tank to reduce the formation of hydrogen sulfide gas. The chemicals are then added to the flash mixer where they are thoroughly mixed with the wastewater.

After the flash mix, the precipitate agglomerates in a flocculating chamber either separate or integral to the settling unit, and is then settled. The overflow from the settling unit generally passes through a filter to remove any fine precipitates. Any excess sulfide must be removed before final discharge. This can be achieved either by aeration or by other chemical oxidation techniques.

Sulfide precipitation is being practiced in the inorganic chemicals industry, mining industry, textile industry, and nonferrous metal processing industry. Most of the Chlor-Alkali industry is applying this technology to remove mercury from its wastewater streams.

Literature citations on the efficiency of sulfide precipitation (5, 6, 7) indicate that most results are in the sub ppm range, and that sulfide treatment is superior to hydroxide treatment for the removal of several trace metals. A recent report concluded that, with no complexing agents in the wastewater, the following effluent quality can be achieved (7).

Metals Concentration	
Cadmium	0.01 mg/l
Copper	0.01 mg/l
Zinc	0.01 mg/l
Nickel	0.05 mg/l
Chromium (total)	0.05 mg/l

Adding ferrous sulfide as a polishing step to remove residual metals appears to be a promising, economical technology. However, there is no full-scale sulfide treatment system as a polishing step operating in the inorganic chemicals industry, and treatability studies conducted by the Agency on chrome pigments wastewater and chlor-alkali (diaphragm cell) wastewater in Phase I showed that sulfide treatment as a polishing step following hydroxide precipitation and clarification did not yield significantly increased toxic metal removals. Therefore, the Agency has not proposed sulfide treatment as an advanced treatment technology option for the Phase II inorganic chemical subcategories.

One cadmium pigments plant is using ferrous sulfide and filtration treatment as a scavenging process to recover cadmium from its process wastewater for reuse. The effluent from the scavenger is discharged without further treatment. Limited data from that plant indicates that the treatment is not performing as well in reducing cadmium discharge levels as lime, clarification, and filtration. We have insufficient information on the operation of that plant to determine if the poor performance is due to improper operation of the ferrous sulfide and filtration treatment or if the poor performance results from other causes.

THE XANTHATE PROCESS

The use of xanthates for the removal of metals from waste streams appears to be a new, promising technology for treating metal-bearing wastewaters. Xanthates contain functional groups capable of forming insoluble complexes with metals, and the sludge so formed can be separated by conventional means.

Xanthates can be generated by mixing starch or cellulose with carbon disulfide in a caustic medium. Three types of xanthates have been proven in bench pilot scale studies to be effective in removing cadmium, chromium (III), copper, iron, lead, mercury, nickel, silver and zinc from industrial waste waters (9-16). These are:

Soluble starch xanthate with a cationic polymer,

Insoluble starch xanthate, and

Fibrous cellulose xanthate

The general removal mechanism is as follows:

$$2\ ROCS(=S)Na + M^{++} = ROCS(=S)_2M + 2Na^+ \qquad (12)$$

Xanthate + metal ion = insoluble metallic xanthate + sodium ions

where R = starch or cellulose

Unlike hydroxide precipitation, this process is reported to be effective in removing metals over a wide pH range of 3 to 11, with an optimum range between 7 and 9.

Brass mill wastewaters, lead battery effluent, circuit board rinse waters, electroless copper plating rinse waters, pyrophosphate electroplating rinse waters, and copper etching rinse waters were studied in a pilot plant with insoluble starch xanthate as the complexing agent (16). This pilot study demonstrated that the xanthates can either be added to a reactor to mix with the wastewaters or be applied as a precoat on a pressure filter (16). Results of these pilot studies showed that metals were reduced to below 50 μg/l (ppb).

Another study indicated cellulose xanthate is as effective as starch xanthate in removing trace metals. The following table summarizes the results of the study with a cellulose xanthate dosage of 90 mg/l and a contact time of 30 minutes (14,15):

	Concentration, mg/l	
Metals	Influent	Effluent
Cadmium	1.35	0.027
Chromium	0.30	0.022
Copper	1.6	0.06-0.14
Iron	3.1	0.08-0.36

Lead	3.9	0.008-0.021
Nickel	2.4	0.077
Zinc	1.0	0.03-0.04

This study also concluded that cellulose xanthate is superior to starch xanthate in terms of sludge settling characteristics, filterability, and handling.

Xanthate may also be used as a complexing agent to prevent the formation of soluble anions from insoluble amphoteric metal hydroxides.

The xanthate process is a relatively new technology, and the reagent compounds are not yet available in commercial quantities. More information is needed on dosage rates in continuous flow operations. Potentially the metals can be recovered by leaching the xanthate complex with nitric acid, but metal recovery has not been demonstrated yet. Sludge disposal problems may arise if the sludge complex is unstable and, if xanthates are to be generated on site, care will be needed in handling the hazardous carbon bisulfide. For these reasons, the xanthate process has not been considered here as an available technology.

ION EXCHANGE

Ion exchange is a chemical reaction between the ions in solution and the ionic sites on an exchange resin. Many natural substances (e.g., soils, proteins, and zeolites) exhibit such exchange characteristics. However, synthetic resins are the predominant ones used for ion exchange applications in modern industrial technology. These resins contain functional groups that can react with the ions in solution. Depending on these functional groups, the resins can be classified into:

Strongly acidic cation exchanger,
Weakly acidic cation exchanger,
Strongly basic anionic exchanger, and
Weakly basic anionic exchanger.

Cation exchangers are capable of exchanging with cations in solution. Strongly acidic cation exchangers contain functional groups such as sulfonates, ($-SO_3H$ and $-SO_3Na$), while weakly acidic exchangers have functional groups derived from carboxylic acids, (-COOH and -COONa).

Anionic exchangers are used to exchange with the anions in solution. In general, strongly basic exchangers contain amine functional groups ($-R_3NOH$ and R_3NCl), and weakly basic exchangers contain ammonia functional groups ($-NH_3OH$ and $-NH_3Cl$).

When the functional groups are used up in the reaction, the resins can usually be regenerated. Cationic resins can be regenerated by sodium chloride, hydrochloric acid, sulfuric acid or sodium hydroxide. Anionic resins are regenerated by sodium hydroxide, ammonium hydroxide, sodium carbonate, sodium chloride, or hydrochloric acid.

The exchanger can either be added to the wastewater in batch operations or packed in a fixed bed or column. Fixed bed is by far the more effective and hence more popular method. The operation generally follows a four-step cycle: exchange (service), backwash, regeneration, and rinse.

During the exchange step, the reaction between the ions in solution and the ionic sites in the resin takes place as the wastewater passes down the bed. The reaction is generally regarded as a result of electrostatic attraction (16). Therefore, the size of the hydrated ion and the charge on the ion are the determining factors for the exchange reaction. A trivalent ion is attracted more strongly than a bivalent ion which is in turn attracted more strongly than a monovalent ion. For ions with the same charge, the smaller hydrated ion is capable of moving closer to the exchange site, and is thus favored.

Many synthetic resins contain functional groups that are selective to certain metals. For example, a resin manufactured by a European company reacts preferentially with mercury (Hg^{++}) and mercuric chloride ($HgCl^{+}$) ions according to the following equations:

$$2RSH + Hg^{++} = RSHgSR + 2H^{+} \qquad (13)$$

Resin + mercury ion = insoluble resin complex + hydrogen ions

$$RSH + HgCl^{+} = RSHgCl + H^{+} \qquad (14)$$

Resin + mercuric chloride ion = insoluble resin complex + hydrogen ions

The exchange reaction is governed by the Law of Mass Action. During the reaction, the affinity of the resin for the two ions is so great that essentially all the mercury or mercury chloride-resin complex formation equilibria are shifted toward the formation of Hg^{++} and $HgCl^{+}$ which are rapidly removed. A 5 ppb residual mercury concentration in the effluent is achieved by this process (18).

After all the exchangeable sites in the resin are used up, the bed is backwashed by passing clean water through to loosen up the bed and to remove any fine particulates that are trapped inside the bed.

After the backwash cycle the resins can be regenerated with the appropriate regenerant.

$$RSHgCl + HCl = RSH + HgCl_2 \qquad (15)$$

Insoluble resin complex = regenerated resin
+ hydrochloric acid + mercuric chloride

One attractive feature of the ion exchange process is that it concentrates the metals in the regeneration step, and thus provides a potential for their recovery. However, if recovery is not feasible, this creates a secondary stream which needs to be treated.

A recent study found that sodium alumino silicates (zeolites) might be a low-cost exchanger that can be discarded after a one-time use (18). This would eliminate the regeneration step. On a batch study with a five-minute contact time, cadmium and mercury were removed to below 10 ppb. Thermodynamic considerations show this exchanger to have a high affinity for cadmium, copper, mercury, nickel, silver, zinc, cesium, and barium.

Ion exchange is a proven technology that can reduce metal concentrations to low levels. However this technology is used only in limited industrial pollution abatement applications where the value of the materials recovered from the backwash offsets the high cost associated with the process. Ion exchange is not used in the Phase II industries. Consequently, ion exchange has not been recommended in this report for BAT technology.

REDUCTION PROCESSES

Many metals can exist in solution in several oxidation states, and it may be necessary to convert from a higher valence state to a lower one in order to apply a given chemical reaction. The classic example is chromium which, as the trivalent chromic ion, will precipitate as the hydroxide in alkaline solution, while the hexavalent chromate or dichromate ion will not. The latter needs to be reduced if precipitation is to occur.

Hexavalent chromium (e.g., $CrO_4^=$ and $Cr_2O_7^=$) is toxic and soluble. The most efficient way of removing this from solution is a two-step process of reduction followed by precipitation.

Chromium (III) is much less toxic than chromium (VI), and forms an insoluble hydroxide which can be removed from solution by settling and filtration.

A number of chemicals are used for the reduction of chromium. Most common are sodium bisulfite, sodium metabisulfite, sulfur dioxide and ferrous salts. The reduction is accomplished readily at low pH with these reagents. Typical reduction reactions are:

$$3SO_2 + Cr_2O_7^{--} + 2H^+ = 2Cr^{+++} + 3SO_4^{--} + H_2O \qquad (16)$$

Sulfur dioxide + dichromate ion = trivalent chromium ion
+ hydrogen ion + sulfates and water

$$3SO_3^{--} + Cr_2O_7^{--} + 8H^+ = 2Cr^{+++} + 3SO_4^{--} + 4H_2O \qquad (17)$$

Sulfite ion + dichromate ion = trivalent chromium ion
+ hydrogen ion + sulfates + water

$$6Fe^{++} + Cr_2O_7^{--} + 14H^+ = 2\ Cr^{+++} + 6\ Fe^{+++} + 7H_2O \qquad (18)$$

Ferrous ion + dichromate ion = trivalent chromium ion
+ hydrogen ion + ferric ion + water

The reduced chromium and the ferric ions produced in the third equation will exist as the soluble sulfate at acid pH's. If the pH is above 5, the reaction rate is drastically reduced, and although dithionite will effect reduction at neutral pH's, it is very costly and its use may be contraindicated.

After the reduction step, lime or caustic soda is added to raise the pH to 8.5-9.0. Trivalent chromium will be precipitated.

$$Cr^{+++} + 3OH^- = Cr(OH)_3 \qquad (19)$$

Trivalent chromium ion = insoluble chromium hydroxide
+ hydroxide ion

The theoretical solubility limit of chromium hydroxide is above 0.02 mg/l (4). It is reported that applying sulfur dioxide to a pigment waste consistently reduces Cr (VI) and Cr(T) to 0.5 mg/l and 1.5 mg/l respectively as 30-day averages (5, 6). By applying ferrous sulfide to a plating waste with an initial Cr(VI) concentration of 128 mg/l and Cr(T) concentration of 153 mg/l, an effluent quality of less than 0.05 mg/l of either species is achieved (8).

A one-step precipitation reduction process using sodium bisulfide was used in a sodium dichromate plant to remove chromium from its wastewater. An effluent quality with less than 1 mg/l Cr(VI), and less than 5 mg/l Cr(T) was reported (20).

One other common reduction process is the application of sodium borohydride to reduce metals in waste streams. Sodium borohydride is a mild but effective reducing agent (20), and is currently used in one chlor-alkali plant to reduce the soluble mercury ion to metallic mercury which is removed from solution by carbon adsorption:

$$4Hg^{++} + BH_4^- + 8\ OH^- = 4Hg + B\ (OH)_4 + 4H_2O \qquad (20)$$

Mercury ion + borohydride ion = insoluble mercury metal
+ hydroxyl ion + borate ion + water

A mercury level of 0.01 mg/l in the final effluent has been reported (20).

Sodium borohydride is also reported to be effective in removing silver, mercury, gold, lead, and cadmium (5). However, this technology is only being applied in limited cases, the cost of the chemical being the major drawback. The cost of sodium borohydride was $19.00 per pound in 1983 (19).

OXIDATION PROCESSES

The oxidation of organic substances is generally carried out by thermal processes such as wet oxidation and incineration, or by biological processes such as the activated sludge process, trickling filters, biodiscs, and aerated lagoons.

Incineration is actually a combination of oxidation and pyrolysis. Both involve chemical changes resulting from heat. Oxidation involves actual reaction with oxygen, while pyrolysis refers to rearrangement or breakdown of molecules at high temperatures in the absence of oxygen. There are five types of incinerators available commercially. These are rotary kiln, multiple hearth, liquid injection, fluidized bed, and pyrolysis (21). A minimum temperature of 1000 degrees C and a residence time of two seconds is required for the reaction to proceed. This process has been shown to be successful in reducing pesticides to harmless molecules (22).

Wet oxidation is a process in which an aqueous waste can be oxidized in the liquid phase in a closed, high-temperature, high pressure vessel. This reduces some of the problems (such as air pollution from exhaust gas), inherent in incineration. Wet oxidation has been used for a variety of wastes including pulping waste and acrylonitrile liquor (23). A reduction in excess of

99.8 percent of some of the toxic pollutants has been reported (24).

Thermal oxidation processes are not expected to have much application in the inorganic chemicals industry, mainly because of the high energy cost required and the low level of organic contamination found in the wastes.

The application of chemical oxidation to industrial wastes is well established for cyanides, sulfite, ammonia, and other harmful species in dilute waste streams (phenols, mercaptans, polysulfides, etc.). Common chemicals used as oxidizing agents included chlorine, hypochlorite, hydrogen peroxide, potassium permanganate, ozone, and chlorine dioxide. Air and oxygen are also used.

The most widely used chemical oxidation technology applicable to the inorganic chemicals industry is the oxidation of cyanide. The oxidation reaction between chlorine and cyanide is believed to proceed in two steps as follows:

$$CN^- + Cl_2 = CNCl + Cl^- \qquad (21)$$

Cyanide + chlorine = cyanogen chloride + chloride ion

$$CNCl + 2OH^- = CNO^- + Cl^- + H_2O \qquad (22)$$

Cyanogen chloride + hydroxyl ion = cyanate ion + chloride ion + water

The formation of cyanogen chloride (CNCl) is essentially instantaneous. The second reaction, the formation of cyanate, is accomplished most rapidly and completely at a pH of 10 or higher (5, 25). A detention time of 30 minutes to two hours is usually allowed.

The cyanates can be further decomposed into nitrogen and carbon dioxide by excess chlorination or acid hydrolysis:

$$2CNO^- + 4OH^- + 3CL_2 = 6Cl^- + 2CO_2 + N_2 + 2H_2O \qquad (23)$$

Cyanate + hydroxyl ion + chlorine = chloride ion + carbon dioxide + nitrogen + water

$$CNO^- + 2H_3O^+ = CO_2 + NH_4^+ + H_2O \qquad (24)$$

Cyanate + hydronium ion = carbon dioxide + ammonium ion + water

The first reaction can be accomplished in about one hour if the pH is adjusted to 8.0-8.5. Acid hydrolysis usually takes place at pH 2-3 and care must be taken to avoid the liberation of the toxic cyanogen chloride as a gas. Hydrolysis is not usually the chosen option.

Other common chemicals used to oxidize cyanide include sodium hypochlorite, ozone, and hydrogen peroxide. The reaction for sodium hypochlorite is essentially the same as for chlorine. For ozone and hydrogen peroxide, the oxidation step proceeds as follows:

$$O_3 + CN^- = O_2 + CNO^- \qquad (25)$$

Ozone + cyanide = oxygen + cyanate ion

$$H_2O_2 + CN^- = CNO^- + H_2O \qquad (26)$$

Hydrogen peroxide + cyanide = cyanate ion + water

The advantage of using these two oxidizing reagents is that no dissolved solids are added to the wastewater. In addition, excess chlorine is not discharged.

A patented process uses hydrogen peroxide and formaldehyde to decompose cyanide at about 120°F. This has the advantage of precipitating cadmium and zinc simultaneously (5).

Laboratory studies in one plant currently practicing alkaline chlorination indicated that the presence of ammonia in the wastewater reduces the efficiency of cyanide removal. It is well known that ammonia reacts with chlorine or hypochlorous acid to form chloramines:

$$NH_3 + HOCl = NH_2Cl + H_2O \qquad (27)$$

Ammonia + hypochlorous acid = monochloramine + water, etc.

$$NH_2Cl + HOCl = NHCl_2 + H_2O \qquad (28)$$

$$NHCl_2 + HOCl = NCl_3 + H_2O \qquad (29)$$

If excess chlorine is added, chloramines can be converted into nitrogen oxide(s):

$$2NH_3 + 4HOCl = N_2O + 4HCl + 3H_2O \qquad (30)$$

This equation is not exact because the final form of nitrogen oxide is believed to be a mixture of nitrous oxide, nitrogen dioxide and nitric oxide.

The treatment of cyanide by chemical oxidation is currently practiced in the following industries:

Inorganic Chemicals (Hydrogen Cyanide Production)

Ore Mining and Dressing (Cyanidation Mills, Froth Flotation Mills)

Plating

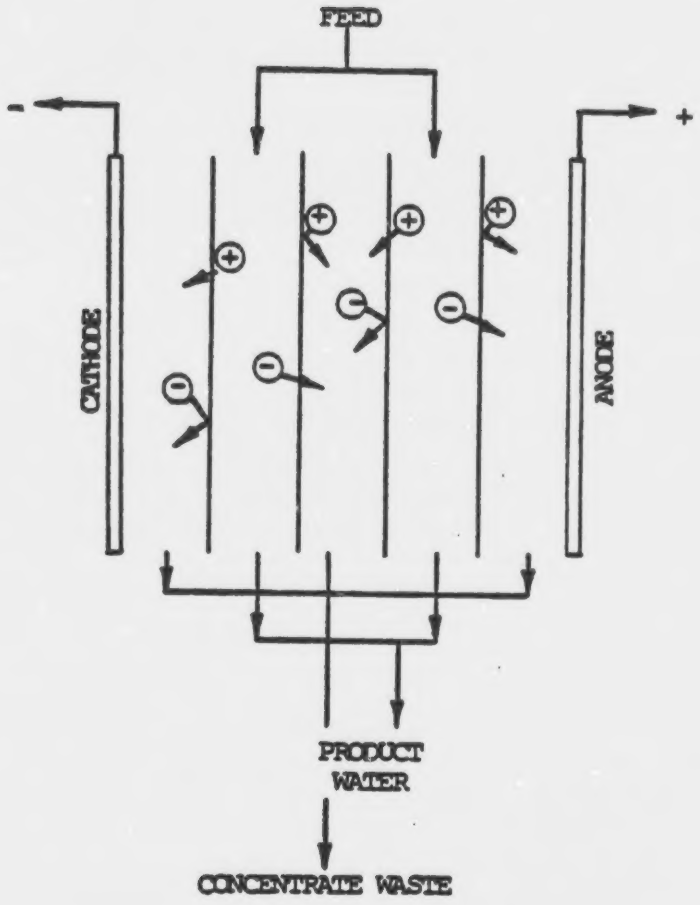
The free cyanide level after treatment is generally below 0.1 mg/l (5). However, cyanide was not detected at significant levels in the Phase II industries and therefore cyanide oxidation was not further considered.

MEMBRANE PROCESSES

Membrane processes have emerged in the last decade as a promising new technology for the treatment of saline water and wastewater. A membrane is a semi-permeable barrier which allows the transport of some molecules (ions) and retains others. The driving force can either be electropotential differences (electrodialysis) or pressure difference (reverse osmosis and ultrafiltration). The major application of these processes has been the desalination of brackish water and sea water. More recently, these have also found application in a number of industries, including:

Mineral Mining (Extraction from brines)
Electroplating
Metal Finishing
Printed Circuit Board Manufacturing
Battery Manufacturing
Pulp and Paper
Food Processing

In electrodialysis, an even number of alternating anion and cation selective membranes are placed between two electrodes. When current is applied the anions are attracted to the anode, and cations are attracted to the cathode. In the process of migration, the cations pass through the cation-permeable membrane and are blocked by the anion-permeable membrane. Likewise, the anions pass through the anion-permeable membrane and are blocked by the cation membrane. This results in alternating paths of purified water and concentrated reject (Figure 7-3).



FEED
-
+
CATHODE
ANODE
PRODUCT
WATER
CONCENTRATE WASTE

Figure 7-3. Electrodialysis process.

TABLE 7-2. COMPARISON OF REVERSE OSMOSIS CONCEPTS

	Packing Density (ft^2/ft^3)	Water Flux at 600 psi (gal/ day/ft^2)	Water Output Per Unit Volume (gal/ day/ft^2)	Sodium Chloride Rejection	Parasitic Pressure Losses (psi)		Useful pH Range	Ease of Cleaning
					Feed Channel	Product Channel		
Plate-and-Frame	150	10	1500	Very good	30	30	2-8	Fair
Large tubes	50	10	500	Very good	50	10	2-8	Very good
Spiral	250	10	2500	Very Good	10	50	2-8	Good to very good
Polyamide hollow fine fibers	5000	1(400 psi)	5000	Fair	10	50	0-12	Fair
Cellulose acetate hollow fine fibers	2500	3(250 psi)	7500	Good	10	50	3-7	Fair

Source: Weber, Physicochemical Processes, 1972.

The electrodialysis membranes are made very thin and are assembled in stacks. The flow path is the active portion of the cells. Pretreatment to remove suspended materials is absolutely essential. Other materials in the waste feed that may lead to membrane fouling include high organic content, calcium sulfate, and certain complex ions such as $ZnCl^-$ which can partially convert the anion membrane to the cation form, with significant loss in system performance (25).

As ionic concentration decreases, the electroconductivity of the water also decreases, making it less efficient to remove the remaining salt. Most operations do not produce a product water of less than 500 mg/l total dissolved solids.

Reverse osmosis (RO) and ultrafiltration (UF) are similar in basic concepts. Both are pressure-driven separation processes that employ high-flux semi-permeable membranes operating under dynamic flow conditions (26). In contrast to electrodialysis, these involve the transport of solvent, not solute, across the membrane.

Osmosis is a process in which solvent from a dilute solution is transported spontaneously across a semi-permeable membrane into a concentrated solution. By applying enough pressure to overcome this osmotic pressure, reverse osmosis, i.e., the passage of solvent from a concentrated solution to a dilute solution through a semi-permeable membrane, occurs. The operating pressure of reverse osmosis units is usually between 350 and 600 psi. Ultrafiltration usually operates at a much lower pressure (5 to 100 psi). The predominant transport mechanism is selective sieving through pores. The membrane retains high molecular weight dissolved solids such as synthetic resins, colloids, and proteins. The upper and lower molecular weight limit is generally defined as 500,000 and 500, respectively.

Membranes are usually fabricated in flat sheets or tubular forms. The most common material is cellulose acetate but other polymers such as polyamides are used. There are four basic module designs: plate-and-frame, tubular, spiral-wound, and hollow fiber. Table 7-2 is a comparison between the various reverse osmosis modules. Membrane processes are effective in removing (concentrating) inorganic and organic substances from a wastestream. Usually extensive pretreatment is required to reduce the suspended solids and control pH. There are uncertainties about operation efficiency, membrane lifetime, rejection specificity, and other factors. If recovery is not feasible, the concentrated reject must be disposed or treated by other methods. The high operating and capital costs limit the widespread application of these technologies. For these reasons, the membrane processes have not been considered as available technologies in the inorganic chemicals industry.

ADSORPTION

Adsorption is a surface phenomenon in which a substance is accumulated on the surface of another substance. Sorption of a solute on a solid surface is widely used in pollution abatement practices. The term "adsorbate" refers to the substance being concentrated, and the term "adsorbent" refers to the material that provides the surface.

Activated carbon is the prevalent adsorbent used. Both inorganic and organic substances are known to be removed effectively by activated carbon. A chlor-alkali plant is currently using activated carbon as a polishing step to remove mercury.

Activated carbon is made by charring basic substrates, such as wood, coke, coal, shell, husks, etc., at 600°C in a controlled atmosphere, where oxygen is kept low by adding carbon dioxide or steam. This process drives out volatiles, leaving a porous carbon lattice in an "activated" state.

Activated carbon can be obtained in powdered and granular form. Powdered carbon is about 50-70 microns in diameter, and 90 percent should pass through a 300-mesh screen. Granular carbon is about 0.1-1 mm in diameter, and because of this is three times more expensive than powdered carbon.

The application involves the passage of the wastewaters through a contact bed. When the bed is exhausted, the carbon is either regenerated or sent to landfill. It is economical for large plants to regenerate the carbon. This can be done either by thermal regeneration in a rotary kiln or multihearth incinerator, or by chemical regeneration by using oxidizing agents such as hydrogen peroxide or acids and bases.

The application of carbon adsorption has been mainly in organic waste treatment. Recently, there are studies indicating the effectiveness of carbon adsorption in removing mercury, cadmium, cyanide, chromium, lead, nickel, zinc, arsenic, and copper (27, 28).

An interesting development in carbon technology is its use after the wastewater is ozonated. This combination (known as Bacteriologically Activated Carbon or BAC) has proved effective in treating otherwise biologically inactive organic compounds. The process involves chemical modification of the organics by the ozone. Maintenance of an aerobic region on the carbon allows a biologically activated film to develop and the modified organics are further treated by a mixed process of biological oxidation and carbon adsorption. The system has the advantage of being a potential add-on to existing BPT systems, and should be cost effective since it has been found that the carbon only needs regeneration at infrequent intervals.

No industrial applications of this technology are known, although research is under way (29).

Bacteriologically Activated Carbon is a very attractive potential BAT technology for the removal of organic toxic pollutants from waste streams, although no application to the industry subcategories studied in Phase II was found.

FLUORIDE REMOVAL

The conventional method of treating fluoride-bearing wastes is to precipitate the fluoride as calcium fluoride by the addition of lime. The reaction is:

$$Ca(OH)_2 + 2F^- = CaF_2 + 2OH^- \qquad (31)$$

Hydrated lime + fluoride ion = insoluble calcium fluoride
+ hydroxyl ion

Using this process alone, it is difficult to remove fluoride to below 8 mg/l due to the solubility of calcium fluoride (5, 30). Adding alum with the lime generally improves the removal efficiency. Fluoride ions are removed as follows:

$$Al(OH)_3 + F^- = Al(OH)_2F + OH^- \qquad (32)$$

Aluminum hydroxide + fluoride ion = aluminum monofluorohydroxide + hydroxyl ion, etc.

$$Al(OH)_2F + F^- = Al(OH)F_2 + OH^- \qquad (33)$$

$$Al(OH)F_2 + F^- = AlF_3 + OH^- \qquad (34)$$

Complexed fluorides are also adsorbed to some extent on the aluminum hydroxide surface and removed in the coagulation process (30). Large amounts of alum (5000 mg/l) are required to reduce the fluoride concentration to below 1 ppm.

Activated alumina has been shown to be effective in removing fluoride and arsenic in wastewater (31) and fluoride from drinking water in municipal water treatment practice (32-35). Typically, the fluoride content of raw water can be reduced from about 8 to 1 ppm (35). Application of activated alumina to high fluoride industrial wastes shows that a low ppm effluent can be achieved (36), although high capital and operating costs generally limit the wide application of this process.

One plant produces a variety of Phase I and Phase II chemicals including nickel fluoborate. Wastewater from nickel fluoborate production is treated together with other fluoride-containing wastewater streams in a conventional fluoride treatment system similar to that described above.

CHLORINE REMOVAL

The removal of residual chlorine (in the form of hypochlorite) in industrial wastewater is normally accomplished by the addition of sulfur dioxide or a related reducing agent such as sodium bisulfite or sodium metabisulfite. Typical reactions are shown in Equations 35 and 36.

$$SO_2 + OCl^- + H_2O = H_2SO_4 + Cl^- \qquad (35)$$

Sulfur dioxide + hypochlorite ion + water = sulfuric acid + chloride ion

$$Na_2SO_3 + OCl^- = Na_2SO_4 + Cl^- \qquad (36)$$

Sodium sulfite + hypochlorite ion = sodium sulfate + chloride ion

Alternatively, hydrogen peroxide, although relatively expensive, may also be used for dechlorination according to Equation 37.

$$H_2O_2 + OCl^- = H_2O + O_2 + Cl^- \qquad (37)$$

Hydrogen peroxide + hypochlorite ion = water + oxygen + chloride ion

Chlorine residuals remaining after the recovery and/or decomposition steps have been taken would be amenable to treatment with reducing agents such as sulfur dioxide, bisulfite, or hydrogen peroxide as described above.

CONCLUSION

This Section has described the theoretical basis for treatment systems considered for application in this industry. The treatment systems selected for application are hydroxide precipitation, settling, and filtration, with chemical reduction of hexavalent chromium and chlorine where those pollutants are found in the wastewater. As demonstrated by descriptions of those technologies and the data presented in Section 8 below, those treatment technologies are applicable to any wastewater containing those pollutants. Therefore, when an industry currently discharges those pollutants with no treatment or inadequate treatment, it is appropriate to transfer the technologies and estimate the effectiveness of the technologies when applied to the new industry based on their demonstrated effectiveness in other industries.

SECTION 7

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SECTION 8

TREATABILITY ESTIMATES AND LONG-TERM DATA ANALYSIS

The Development of Treatability Estimates

Preliminary Analysis

The review of technological treatment options applicable to the removal of toxic pollutants has led to the conclusion that the particular contaminants found in the raw process wastewaters of the subject industries can be effectively controlled by the proper application of fairly well-known and demonstrated techniques. In order to proceed from a general discussion and description of techniques to a detailed evaluation for each subcategory of the levels of removal that can be expected, a summary is now presented of selected treatability data for the 13 toxic metals.

The treated wastewater concentrations and removal efficiencies reported in the literature are assumed to represent the best performance characteristics that can be obtained under the specified operating conditions. The treatment technologies considered can thus be assigned a set of optimum conditions and best performance estimates for removal of the particular toxic metals that are amenable to treatment. Taking each metal in turn, Tables 8-1 through 8-10 give the initial and final concentrations, the removal efficiencies, and the pH conditions for different treatment technologies. The best performance estimates for metal removal are derived from the tabulated data and are utilized in turn as the bases for making estimates of average achievable performance. The sequence of analytical steps is:

1. Review and analyze applicable performance data.
2. Estimate best performance under optimum treatment conditions.
3. Estimate average achievable performance under expected industrial operating conditions.

The third step involves the consideration of treatment system variables under full-scale operating conditions in industrial situations where the design objective would be the simultaneous removal of several waste load constituents. Each industry designs for maximum removal and/or recovery of the major process-related wastewater pollutants and utilizes an appropriate technology which is both reliable and cost-effective. Optimum treatment conditions for the removal of a particular pollutant can rarely be achieved consistently and any given set of conditions will be somewhat less than optimum for most, if not all, of the treatable constituents. In any well-operated production facility, the normal variations in production rates, raw material quality, the desired product mix in some cases, and contact water use requirements may cause severe hydraulic and pollutant load input excursions which at best can be moderated by effective equalization in the treatment system. This is considerably less of a problem in batch treatment than with a continuously operating system. The latter requires continuous feedback monitoring for pH control and chemical dosage in order to maintain the effluent quality within acceptable limits for a number of parameters. Under continuous operating conditions, the long-term averages derived from the actual treated effluent monitoring data (NPDES, etc.) would equate to what has been identified in Step 3 above as the estimated long-term average achievable performance using the same general treatment technology.

The estimated ranges of average achievable performance are presented in Table 8-11. In formulating the regulations, these values were used as long-term averages in cases where there were insufficient data from sampling or long-term monitoring of the actual industry discharges.

Statistical evaluation of long-term monitoring data is described in the subsections which follow, and the results are presented in Appendix A where various derivative quantities such as long-term averages and standard deviations are tabulated.

Final Analysis

Following publication of the proposed Phase I regulations on July 24, 1980 (45 FR 49450) additional data on performance of the BPT and BAT options for several subcategories were evaluated and eventually incorporated into the basis for the final regulations. The sources of additional data which are also applicable to the subcategories considered here include the following:

A. Treatability Study for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-80-103, July, 1980.

B. Industry comments on the proposed Phase I regulations - The written comments received by EPA as well as comments given orally at the public hearing on proposed pretreatment standards (October 15, 1980) are part of the official public record of the Phase I rulemaking. The comments are summarized and responses are given

TABLE 8-1. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - ANTIMONY AND ARSENIC REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Antimony					
Lime/Filter	11.5	0.6	0.4	28	1
Ferric chloride/Filter	6.2	0.5	0.2	65	1
Alum/Filter	6.4	0.6	0.2	62	1
Arsenic					
Lime Softening	-	0.2	0.03	85	2, 3
Sulfide/Filter	6-7	-	0.05	-	2, 3
Lime (260 mg/l)/Filter	10.0	5.0	1.0	80	4
Lime (600 mg/l)/Filter	11.5	5.0	1.4	72	4
Ferric sulfate	5-7.5	0.05	0.005	90	5
Ferric sulfate	6.0	5.0	0.5	90	4
Lime/Ferric Chloride/ Filter	10.3	3.0	0.05	98	2, 3
Activated alumina (2 mg/l)	6.8	0.4-10	<0.4	96-99+	6
Activated carbon (3 mg/l)	3.1-3.6	0.4-10	<4.0	63-97	6
Ferric Chloride	-	0.3	0.05	98	2, 3
Ferric Chloride	-	0.6-0.9	<0.13	-	2, 3

TABLE 8-2. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - BERYLLIUM AND CADMIUM REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Beryllium					
Lime/Filter	11.5	0.1	0.006	99.4	1
Cadmium					
Lime (260 mg/l)/Filter	10.0	5.0	0.25	95	4
Lime (600 mg/l)/Filter	11.5	5.0	0.10	98	4
Lime Softening	5-6.5	0.44-1.0	0.008	92-98	7
Lime/Sulfide	8.5-11.3	0.3-10	0.006	98+	8
Ferrous Sulfide (Sulfex)	8.5-9.0	4.0	<0.01	99+	7,9,10
Ferrite coprecipitation/ Filter	neutral	240	0.008	99+	11

TABLE 8-3. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - COPPER REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Lime/Filter	8.5-9.0	3.2	0.07	98	7
Lime (260 mg/l)/Filter	10.0	5.0	0.4	92	4
Lime (600 mg/l)/Filter	11.5	5.0	0.5	91	4
Ferric sulfate/Filter	6.0	5.0	0.3	95	4
Lime	>8.5	10-20	1-2	90	2,3
Lime	9.5	3.0	0.2	93	12
Alum	6.5-7.0	3.0	0.2	93	12
Lime/Sulfide	5.0-6.5	50-130	<0.5	-	8
Ferrous sulfide (Sulfex)	8.5-9.0	3.2	0.02	99	7
Ferrous sulfide (Sulfex)	8.5-9.0	4.0	0.01	99+	7,9,10
Ferrite Coprecipitation/ Filter	-		0.01	99+	11

TABLE 8-4. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - CHROMIUM III AND CHROMIUM VI REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Chromium					
Lime (260 mg/l)/Filter	10.0	5.0	0.1	98	4
Lime (600 mg/l)/Filter	11.5	5.0	0.1	98	4
Reduction/Lime	7-8	140 (as Cr VI)	1.0	—	2, 3
Reduction/Lime	7-8	1300 (as Cr VI)	0.06 CrIII	—	2, 3, 13
Lime Softening	10.6-11.3	—	0.15	98+	14
Lime/Filter	7-9	—	0.05	—	15
Lime	9.5	15	0.1	—	12
Lime	9.5	3.2	<0.1	—	12
Ferrite coprecipitation/ Filter	—	25	0.01	—	11
Ferric sulfate	6.5-9.3	—	—	98+	14
Ferric sulfate/Filter	—	5.0	0.05	99	4
Chromium VI					
Activated carbon (pulverized, Pittsburgh type RC)	3.0	10	1.5	85	16
Same as above	2.0	10	0.4	96	16
Activated carbon (granular)	6.0	3	0.05	98	4
Ferrite coprecipitation	—	0.5	not detectable	—	11
Sulfur dioxide reduction	—	—	0.01-0.1	—	2, 3
Bisulfite reduction	—	—	0.05-1.0	—	2, 3

TABLE 8-5. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - LEAD REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Lime (260 mg/l)	10.0	5.0	0.25	95.0	4
Lime/filter	8.5-9.0	189	0.1	99.9	11
Lime (260 mg/l)/Filter	10.0	5.0	0.075	98.5	4
Lime (600 mg/l)/Filter	11.5	5.0	0.10	98.0	4
Ferrous sulfate/Filter	6.0	5.0	0.075	98.5	4
Sodium hydroxide (1 hour settling)	5.5	—	1.6	—	3
Sodium hydroxide (24 hour settling)	7.0	—	0.04	—	3
Sodium hydroxide/Filter	10.5	1700	0.60	99+	17
Sodium carbonate/Filter	10.1	1260	0.60	99+	17
Sodium carbonate/Filter	6.4-8.7	10.2-70.0	0.2-3.6	82-99+	3
Sodium carbonate/Filter	9.0-9.5	5.0	0.01-0.03	99+	2,3
Ferrous sulfide (Sulfex)	8.5-9.0	189	0.1	99.9	7
Ferrite coprecipitation/ Filter	—	480	0.01-0.05	99.9	11

TABLE 8-6. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - MERCURY II REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Sulfide	-	0.3-50.0	0.01-0.12	-	2,3
Sulfide	10.0	10.0	1.8	96.4	18
Sulfide/Filter	5.5	16.0	0.04	99	18
Sulfide/Filter	4.0	36.0	0.06	99.8	18
Sulfide/Filter	5.8-8.0	0.3-6.0	0.01-0.125	87-99.2	18
Ferrite coprecipitation/ Filter	-	6.0-7.4	0.001-0.005	99.9	11
Activated Carbon	-	0.01-0.05	<0.0005	-	2,3
Activated Carbon/Alum	-	0.02-0.03	0.009	-	14
Activated Carbon	-	0.06-0.09	0.006	-	18

TABLE 8-7. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - NICKEL REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Lime	8.5-9.0	75	1.5	98	8
Lime (260 mg/l)/Filter	10.0	5.0	0.3	94	4
Lime (600 mg/l)/Filter	11.5	5.0	0.15	97	4
Caustic Soda/Filter	11.0	-	0.3	-	17
Ferrous sulfide (Sulfex)	8.5-9.0	75	0.05	99.9	7,10
Ferrite coprecipitation	-	1000	0.20	99.9	11

TABLE 8-8. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - SILVER REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Sodium hydroxide	9.0	54	15	72	19
Ferric sulfate (30 mg/l)	6-9	0.15	0.03-0.04	72-83	14
Lime Softening	9.0-11.5	0.15	0.01-0.03	80-93	14
Chloride precipitation (alkaline chlorination in the presence of cyanide)	-	105-250	1.0-3.5	97+	2,3
Ferric chloride/Filter	6.2	0.5	0.04	98.2	1
Sulfide precipitation	5-11	-	-	very high	2,3

TABLE 8-9. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - SELENIUM AND THALLIUM REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Selenium					
Ferric chloride/Filter	6.2	0.1	0.03	75	1
Ferric chloride/Filter	6.2	0.05	0.01	80	1
Alum/Filter	6.4	0.5	0.26	48	1
Ferric sulfate	5.5	0.10	0.02	82	20
Ferric sulfate	7.0	0.10	0.03	75	20
Lime/Filter	11.5	0.5	0.3	35	1
Lime/Filter	11.5	0.06	0.04	38	1
Thallium					
Lime/Filter	11.5	0.5	0.2	60	1
Ferric chloride/Filter	6.2	0.6	0.4	30	1
Alum/Filter	6.4	0.6	0.4	31	1

TABLE 8-10. WASTE WATER TREATMENT OPTIONS AND PERFORMANCE DATA SUMMARY - ZINC REMOVAL

Treatment Technology	pH	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal (%)	References
Lime/Filter	8.5-9.0	3.6	0.25	93	7
Lime (260 mg/l)	10.0	5.0	0.85	83	4
Lime (260 mg/l)/Filter	10.0	5.0	0.80	84	4
Lime (600 mg/l)	11.5	5.0	0.35	93	4
Lime (600 mg/l)/Filter	11.5	5.0	1.2	77	4
Lime/Filter	-	16	0.02-0.23	-	11
Sodium hydroxide	9.0	33	1.0	97	19
Sulfide	-	42	1.2	97	11
Ferrous sulfide (Sulfex)	8.5-9.0	3.6	0.02	99+	7,10
Ferrite coprecipitation	-	18	0.02	99+	11

TABLE 8-11. ACHIEVABLE LONG-TERM AVERAGES FOR THE APPLIED TECHNOLOGIES

	Final Concentrations (mg/l)						
	Lime + Settling	Lime + Filter	Sulfide + Filter	Ferrite Coprecipitation + Filter	Soda Ash + Settling	Soda Ash + Filter	Alum
Antimony, Sb	0.8-1.5	0.4-0.8					
Arsenic V	0.5-1.0	0.5-1.0	0.05-0.1				
Beryllium, Be	0.1-0.5	0.01-0.1					
Cadmium, Cd	0.1-0.5	0.05-0.1	0.01-0.1	<0.05			
Copper, Cu	0.5-1.0	0.4-0.7	0.05-0.5	<0.05			
Chromium III, Cr^{+3}	0.1-0.5	0.05-0.5		0.01			
Lead, Pb	0.3-1.6	0.05-0.6	0.05-0.4	0.20	0.4-0.8	0.1-0.6	
Mercury II, Hg			0.01-0.05	<0.01			
Nickel, Ni	0.2-1.5	0.1-0.5	0.05-0.5				
Silver, Ag	0.4-0.8	0.2-0.4	0.05-0.2				
Selenium, Se	0.2-1.0	0.1-0.5					
Thallium, Tl	0.2-1.0	0.1-0.5					0.2-0.5
Zinc, Zn	0.5-1.5	0.4-1.2	0.02-1.2	0.02-0.5			

(continued)

TABLE 8-11 continued

	Final Concentrations (mg/l)			
	Ferric Chloride	Activated Carbon	Bisulfite Reduction	Lime/$FeCl_2$ Filter
Arsenic V, As	0.05-0.5	0.3		0.02-0.1
Chromium VI, Cr^{+6}		0.1	0.05-0.5	
Mercury II, Hg		0.01		
Silver, Ag	0.05-0.1			
Selenium, Se	0.05-0.1			
Thallium, Tl	0.7			

TABLE 8-12. INDUSTRIAL WASTE WATER TREATMENT SYSTEM PERFORMANCE -- SUMMARY OF EFFLUENT CONCENTRATION DATA ON TOXIC METALS(1)

	Lime/Clarification(2)		Lime/Filtration(2)		Sulfide/Filtration(3)	
	(mg/l)	Source(4)	(mg/l)	Source(4)	(mg/l)	Source(4)
Antimony	0.18	PM(5)	ND		0.23	CAM(6)
Arsenic	0.080	NFM(5)	0.30	CP(7)	0.17	CAM(9)
			0.038	CS(8)	0.096	CAM(6)
Beryllium	ND		ND		ND	
Cadmium	0.060	TDS(10)	0.076	MF(11)	ND	
	0.080	NFM(5)				
	0.12	MF(11)				
Mercury	ND		ND		0.020	CAM(9)
					0.022	CAM(12)
					0.036	CAM(9)
					0.057	CAM(13)
Selenium	ND		ND		ND	
Silver	ND		ND		0.070	CAM(9)
Thallium	ND		ND		ND	
Chromium III	0.040	IS(5)	0.037	CP(15)	ND	
	0.050	NFM(5)	0.046	TDC(15)		
	0.050	CAD(14)	0.072	SDC(18)		
	0.070	TTS(10)	0.20	SDC(15)		
	0.071	CAD(15)	0.28	MF(11)		
	0.072	TDC(16)	0.33	CP(7)		
	0.080	TM(5)	0.44	CP(21)		
	0.15	MF(11)				
	0.18	TDC(15)				
	0.26	SDC(15)				
	0.35	CAD(17)				
	0.36	IS(5)				
	0.43	CP(15)				
	0.81	SDC(15)				
	1.8	IS(5)				
	0.15 median		0.20 median		NA	
	0.32 average		0.20 average			

	Lime/Clarification(2)		Lime/Filtration(2)		Sulfide Filtration(3)	
	(mg/l)	Source(4)	(mg/l)	Source(4)	(mg/l)	Source(4)
Copper	0.030	IS(5)	0.035	CP(7)	0.033	CAM(6)
	0.030	CAD(14)	0.13	CP(21)	0.056	CAM(9)
	0.038	OMD(5)	0.17	CS(15)	0.24	CAM(17)
	0.060	OMD(5)	0.23	CS(15)	0.43	CAM(17)
	0.070	NFM(5)	0.25	IS(5)		
	0.070	SEP(5)	0.37	MF(11)		
	0.080	OMD(5)	0.90	MF(11)		
	0.090	OMD(5)				
	0.10	OMD(5)				
	0.14	MF(11)				
	0.54	CAD(17)				
	0.70	NFM(5)				
	1.1	CS(15)				
	1.5	CS(15)				
	0.085 median		0.23 median		NA	
	0.32 average		0.30 average			
Lead	0.017	HF(19)	0.038	MF(11)	0.032	CAD(13)
	0.10	MF(11)	0.11	CP(7)	0.12	CAM(9)
	0.15	OMD(5)	0.41	CP(21)	0.16	CAM(6)
	0.19	NFM(5)			0.46	CAD(15)
	0.20	NFM(5)				
	0.15 median		NA		NA	
	0.13 average					

(Continued)

TABLE 8-12 continued

	Lime/Clarification(2) (mg/l)	Source(4)	Lime/Filtration(2) (mg/l)	Source(4)	Sulfide/Filtration(3) (mg/l)	Source(4)
Nickel	0.020	IS(5)	0.090	SDC(18)	0.022	CAM(9)
	0.050	CAD(14)	0.11	CS(15)	0.074	CAM(6)
	0.10	NFM(5)	0.13	CS(15)		
	0.17	HF(19)	0.19	NS(15)		
	0.20	CS(15)	0.20	CS(8)		
	0.20	SDC(18)	0.59	MF(11)		
	0.25	CS(15)	0.80	NS(20)		
	0.26	CAD(17)				
	0.31	MF(11)				
	0.33	IS(5)				
	0.50	NFM(5)				
	1.4	NS(15)				
	0.23 median		0.19 median		NA	
	0.32 average		0.30 average			

	Lime/Clarification(2) (mg/l)	Source(4)	Lime/Filtration(2) (mg/l)	Source(4)	Sulfide/Filtration(3) (mg/l)	Source(4)
Zinc	0.020	OMD(5)	0.018	CS(8)	0.090	TM(5)
	0.040	OMD(5)	0.058	CP(7)	0.13	CAM(9)
	0.040	FI(5)	0.11	SDC(18)	0.15	CAM(6)
	0.10	CAD(14)	0.25	MF(11)		
	0.11	TM(5)	0.57	MF(11)		
	0.15	TDS(10)				
	0.20	NFM(5)				
	0.24	IS(5)				
	0.25	IS(5)				
	0.35	OMD(5)				
	0.39	MF(11)				
	0.54	CAD(17)				
	0.55	HF(19)				
	0.60	NFM(5)				
	8.2	PM(5)				
	0.20 median		0.11 median		NA	
	0.78 average		0.20 average			

NOTES:

(1) Influent or raw waste concentrations of metals are at treatable levels; i.e., higher than the corresponding treatability ranges given in Table 8-11. All effluent concentrations are measured off treatment and are expressed as total (dissolved plus suspended) for each metal.

(2) Lime/Clarification and Lime/Filtration treatment means equalization of raw waste influent stream(s) followed by alkaline precipitation using lime or caustic soda, solids removal by sedimentation or clarification, and either discharge of the clarified effluent directly or discharge of the filtrate after passage of the clarified effluent through a dual media filter or its equivalent.

(3) Sulfide/Filtration refers to a direct treatment of the equalized raw waste influent by sulfide addition (usually in the form of sodium sulfide or bisulfide) under conditions ranging from pH 5 to 11 followed by settling and/or filtration by filter press or activated carbon column.

(4) Source Codes:

CAD	Chlor-Alkali, Diaphragm Cells	IS	Iron and Steel	SEP	Steam Electric Power Generating
CAM	Chlor-Alkali, Mercury Cells	MF	Metal Finishing (including electroplating)	SDC	Sodium Dichromate
CS	Copper Sulfate	NFM	Nonferrous Metals	TDC	Titanium Dioxide - Chloride Process
CP	Chrome Pigments	NS	Nickel Sulfate	TDS	Titanium Dioxide - Sulfate Process
FI	Foundry Industry	OMD	Ore Mining and Dressing	TM	Textile Mills
HF	Hydrofluoric Acid	PM	Paint Manufacturing		

(5) U.S. Environmental Protection Agency, Treatability Manual, Vol. III, Technologies for Control/Removal of Pollutants, EPA 600 8-80 042 c, July, 1980.

(6) Phase I DD, Table 11-16 (21).

(7) Phase I DD, Table 16-9 (21).

(8) Phase I DD, Table 21-11 (21).

(Continued)

TABLE 8-12 continued

NOTES: continued

(9) Olin Corporation, Chemicals Group, Charleston, TN. Letter to Mr. Elwood E. Martin, U.S. EPA, Effluent Guidelines Division, Washington, D.C., October 20, 1980. Maximum likelihood estimates of the long term averages from Olin mercury treatment effluent data by Jacobs Engineering Group, Inc.

(10) Phase I DD, Table 14-30 (21).

(11) Hamilton Standard, Division of United Technologies Corp., Windsor Locks, CT. Letter to Mr. Richard Kinch, U.S. EPA, Effluent Guidelines Division, Washington, D.C., November 25, 1980. Tabulations of statistical parameters derived from historical data on the metal finishing industry.

(12) The Chlorine Institute, Inc., New York, N.Y. Letter to Mr. G. E. Stigall, U.S. EPA, Effluent Guidelines Division, Washington, D.C., May 28, 1979. Attachment "C", a tabular summary of mercury treatment effluent data.

(13) PPG Industries, Inc., Pittsburgh, PA. Letter to Mr. Elwood E. Martin, U.S. EPA, Effluent Guidelines Division, Washington, D.C., January 2, 1981. Maximum likelihood estimates of the long term averages from PPG mercury and lead treatment effluent data by Jacobs Engineering Group, Inc.

(14) Phase I DD, Table 11-37 (21).

(15) U.S. Environmental Protection Agency, Treatability Studies for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-80/103, July, 1980. Maximum likelihood estimates of long term averages from treatability data by Jacobs Engineering Group, Inc.

(16) Phase I DD, Table 14-12 (21).

(17) Diamond Shamrock Corporation, Dallas, TX. Letter to Mr. Elwood E. Martin, U.S. EPA, Effluent Guidelines Division, Washington, D.C., October 22,1980. Tabular summary of highest values from treatment effluent during one month of monitoring.

(18) Phase I DD, Table 18-13 (21).

(19) Phase I DD, Table 12-22 (21).

(20) Phase I DD, Table 22-10 (21).

(21) Phase I DD, Appendix A (21).

ND = No data available

NA = Not applicable

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in "Responses to Public Comments, Proposed Inorganic Chemicals Manufacturing Effluent Guidelines and Standards," which is a part of the Record for that rule. Invidivual comment documents or letters are cited in this report where they are used as sources of information.

C. Treatability Manual, Volume III, Technologies for Control/Removal of Pollutants, EPA 600/8-80-042c, July, 1980.

Table 8-12 presents tabular summaries of the available industry treatment performance data for most of the priority metals. These include estimated long-term averages in cases where there were sufficient data given to utilize the Maximum Likelihood Estimation method for calculating statistical parameters as indicated in the footnotes. Overall arithmetic medians and averages are also given for metals where five or more individual data sets were available.

An industry long-term average effluent concentration was then estimated for each pollutant/treatment option combination for which sufficient data were available. Plants presently practicing filtration are generally those with higher raw waste concentrations of metals in comparison to plants which can achieve adequate treatment without filtration. This tends to reduce the observed differences in performance with and without filtration and, therefore, understates the potential benefit of adding filtration to a particular lime/settling system. The estimated achievable long-term average concentrations, as shown in Table 8-13, generally fall within the estimated range of the corresponding long-term averages in Table 8-11 which were derived from literature data. Thus, there is substantial agreement between the two sets of estimates and there is good reason to conclude that the lower limits of the treatability ranges in Table 8-11 are achievable long-term averages for the inorganic chemicals industry. The metal regulations are based on the estimated achievable long-term average concentrations in Table 8-13 in cases where there are insufficient industry-specific performance data available. The numerical limitation in each case was obtained by multiplying the long-term average concentration by the model plant unit flow rate and an appropriate variability factor. The variability factors are selected to represent as accurately as possible the actual full-scale treatment system's variability under normal operating conditions.

It is understood that in each subcategory plant treatment system conditions, particularly where chemical precipitation is involved, are usually optimized for the removal of only one metal. Other metals may be removed incidentally under the same conditions although their removal efficiencies may not be optimal. An example is the prevalent use of sulfide precipitation/filtration technology for the removal of mercury. The precipitation is normally carried out under neutral to moderately-acid conditions in order to limit the amount of residual sulfide in the system and, depending on specific raw waste characteristics, to obtain desirable solid properties for filtration. Under these conditions, the incidental removals of other metals such as nickel and zinc are not at their maximum efficiencies, but are still effective.

The industry performance data summarized in Table 8-12 for many of the toxic metal/treatment combinations express an observed incidental removal rather than an optimum removal. This provides an empirical basis for estimating practical control levels for metals under off-optimum pH conditions in either alkaline precipitation or sulfide precipitation systems.

Selection of Toxic Metal Control Parameters

Control Parameters for Hydroxide Precipitation

Section 7 of this report describes hydroxide precipitation as the most widely-used technology for removing trace metals from wastewater. Out of the thirteen toxic metal pollutants, two have hydroxide/oxide solubilities independent of the 1-14 pH range (selenium and thallium) and two have minimum hydroxide/oxide solubilities over a wide pH range (antimony at pH 2-10.4 and mercury at pH 4-12). Arsenic is removable by precipitation with lime (probably as calcium arsenate) in the presence of excess calcium ion under neutral to alkaline conditions. As shown in Tables 8-1 and 8-9, removals of antimony and selenium can also be accomplished using excess lime. The mechanism probably is similar to the removal of arsenic, i.e., as the calcium salt of antimony and selenium. The remaining eight toxic metals have minimum hydroxide/oxide solubilities only over relatively narrow pH ranges (see Figure 7-1). Lead may also be effectively treated with carbonate (soda ash, Na_2CO_3) to form insoluble basic lead carbonate precipitates.

It is clear from the range of optimum pH's illustrated in Figure 7-1 that no single pH exists which can effectively remove all eight of these metals. Because they rarely occur at treatable levels and, therefore, rarely require removal, beryllium, silver, mercury and thallium can be eliminated from the selection of an optimum pH range for each group.

Table 8-14 indicates that control of any metal of Group A in the 8.5 - 9.5 pH range should control the other members of the group.

TABLE 8-13. ESTIMATED ACHIEVABLE LONG TERM AVERAGE CONCENTRATIONS FOR PRIORITY METALS WITH TREATMENT OPTIONS

Toxic Metal	Lime/Clarification (mg/l)	Lime/Filtration (mg/l)	Sulfide/Filtration (mg/l)
Antimony	ID(1)	ND(2)	ID
Arsenic	ID	ID	0.15
Beryllium	ND	ND	ND
Cadmium	0.10	ID	ND
Chromium	0.32	0.16	ND
Copper	0.40	0.30	0.20
Lead	0.15	ID	0.10
Mercury	ND	ND	0.034
Nickel	0.40	0.30	ID
Selenium	ND	ND	ND
Silver	ND	ND	ID
Thallium	ND	ND	ND
Zinc	0.80	0.20	0.12

(1) ID: Insufficient data for a reliable estimate

(2) ND: No data available

TABLE 8-14. THEORETICAL SOLUBILITIES OF TOXIC METAL HYDROXIDES/OXIDES AT VARIOUS pH VALUES

pH	8.5	9.5	10.5	11.5
Metal	Concentration (mg/1)			
Group A				
Cr^{+++}	0.030 (1)	0.20	1.0	9.0
Cu^{++}	0.00010	0.000080 (1)	0.00050	0.0020
Pb^{++}	8.0	0.50 (1)	4.0	>10
Zn^{++}	0.60	0.070 (1)	0.50	3.0
Group B				
Cd^{++}	>10	1.0	0.010	0.0010 (1)
Ni^{++}	1.0	0.010	0.0010 (1)	0.010

(1) Lowest value

Control of any metal of Group B in the 10.5 - 11.5 pH range should control the other members of the group. Control of metals from different groups will depend on the details of each case. Possible approaches to controlling metals from different groups might involve the use of the intermediate 9.5 - 10.5 pH range or the control of one metal in one group when the theoretical solubilities of the metal or metals in the other group are low throughout the 8.5 - 11.5 pH range.

Control Parameters for Sulfide Precipitation

Section 7 of this report describes sulfide precipitation as potentially superior to hydroxide treatment for the removal of several toxic metals. Sulfide precipitation has been applied in mercury removal. Figure 7-2 points out that mercury is the most insoluble of the priority metal sulfides and that the solubilities of the metal sulfides are strongly dependent upon pH. Operation of sulfide precipitation in the neutral or slightly alkaline range should result in acceptable removal of all priority metal sulfides as well as minimizing the problem of hydrogen sulfide evolution. Soluble polysulfide formation can be prevented by avoiding the very alkaline pH range and by close control of excess sulfide. These data suggest that sulfide precipitation might be used as a polishing treatment to enhance metals removal to very low concentrations in other industries. However, in the Phase I project, we conducted treatability studies (Treatability Study for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-80-103, July, 1980) to determine the effectiveness of sulfide treatment as a polishing step for chlor-alkali(diaphragm cell) and chrome pigments wastewater treatment. Both subcategories have wastewaters similar to those encountered in the Phase II industries. That treatability study showed that sulfide treatment is not significantly more effective in toxic metal pollutant removal than lime precipitation, clarification, and filtration in the inorganic chemicals industry. Hence, we did not propose the use of sulfide treatment as a polishing step in Phase II because available data shows it does not provide significant improvement over lime precipitation, clarification, and filtration.

The Use of Historical Pollutant Data

Determination of Effluent Limitation Guidelines Based Upon Historical Performance

In cases where there has been long-term monitoring of the pollution levels in the effluent stream discharged by a plant, it is possible to assess in-plant treatment performance through analysis of historical data that has been collected for this purpose. The propriety of standards constructed from data collected from a single plant performance is, of course, dependent on the plant's current performance in relation to the performance of other plants in the manufacturing subcategory. As economically feasible alternative wastewater treatment technologies become available, pollutant discharge guidelines should be reviewed and revised to reflect these advances.

Statistical analysis of historical monitoring data is required to assess a plant's ability to discharge within set guidelines. To perform this analysis certain assumptions must be made regarding the nature of applicable statistical or probabilistic models, the constancy of the operation of the treatment facility, and the quality of the monitoring methods.

The statistical analyses contained in this development document belong to either of two principal types: those for daily observations of pollutant concentrations, and the others for 30-day average pollutant levels.

Tables in Appendix A provide a summary of traditional descriptive measures, i.e., number of observations(No), mimima(Min), arithmetic average(Avg), maxima(Max), and coefficient of variation(CV). In addition, a descriptive statistic, the variability factor, pertinent to the development of performance standards for pollution monitoring, is included. These tables, prepared for both daily measurements as well as for 30-day averages, are statistical summaries derived from data offered by industry in response to Section 308-Questionnaires, and offered in comments on the proposed Phase I and Phase II re gulations. Data in these tables are representative of currently achieved pollutant discharge performance levels in the several plants presented.

Formulation of variability factors to be used in determination of effluent limitations guidelines based upon historical performance was accomplished by employing standard statistical analysis from the data resulting from long-term monitoring of effluent stream discharges from plants in the inorganic chemical manufacturing subcategories. In the following paragraphs are presented details of the theory and derivation of these statistical procedures, and of the resulting formulae which relate variability factors to estimated long-term parameter averages, standard deviations, coefficients of variation, and "Z-values" computed from the normal probability distribution. These details are given both for the analysis applying to daily maxima criterion and for that applying to 30-day averages.

The term "variability factor" refers to the multiple of the long-term average which is used in formulating performance standards. This factor allows for variation in pollution level measurements due to sampling error, measurement error, fluctuations in the amount of the pollutant in raw materials, and other process variations.

In the recording of actual data, as reported by industrial point sources in their responses to Section 308 Questionnaires, certain data values were entered as "less than" detectability limits. In these cases, the set of monitoring data has been "censored" in the process of data recording since only the threshold value has been retained (i.e., if a pollutant concentration was reported as <0.050 mg/l, the value of 0.050 mg/l was used). In the statistical analysis of monitoring data, censored values were included with measured values in the sample. This practice provides a reasonable approach, both for assessing industry's capability to perform and environmental concerns for valid pollutant limitations.

First, since censoring was done only for "less than" bounds, any bias from their inclusion would cause a slight increase in the long-term average, moderately affecting (in the direction of leniency toward industry) the estimate of long-term average pollution levels.

On the other hand, the use of censored values combined with measured values tends to reduce the variability slightly (or in the direction of less leniency toward industrial point sources). For illustration, if the sample consisted solely of censored values, the estimated long-term average might be slightly overstated. Nevertheless, the point source should have no difficulty with the threshold or detectability limit as a performance guideline, since none of the historical data exceeded that limit.

Statistical analysis of influent and effluent data submitted during the comment period by cadmium pigments producers is described in detail in Section 11 below. Statistical analysis of data from a treatability study we conducted at a zinc chloride manufacturing plant is described in detail in Section 16 below.

Assumptions Concerning Daily Pollutant Level Measurement

In the formulation and calculation of the following performance standards, individual sample measurements of pollutant levels were assumed to follow the lognormal distribution, a well known and generally accepted statistical probability model used in pollution analyses. Under this assumption the logarithms of these measurements follow a normal probability model. It was also assumed that monitoring at a given plant was conducted responsibly and in such a way that resulting measurements can be considered statistically independent and amenable to standard statistical procedures. A final assumption was that treatment facilities and monitoring techniques had remained substantially constant throughout the monitoring period.

As an indication of the propriety of assuming a lognormal distribution for daily measurements, the plot of the cumulative distribution of logarithms of daily effluent concentration data on normal probability paper is illustrated in Figure 8-1.

The linearity of the cumulative plot indicates the degree to which actual monitoring data are in agreement with the theoretical lognormal model for their distribution.

In addition, Figure 8-2, also demonstrates the validity of the lognormal assumption for daily data.

In the analysis of daily data, the inherent variability of measured pollutant levels in the effluent stream from inorganic chemical manufacturing processes must be incorporated in calculating upper limits for daily pollutant discharge levels. Even plants exercising good treatment and control may experience some days when atypically high levels of pollutants are present in their treated wastewater streams. Such high variations may be due to a variety of factors, such as short-term maladjustments in treatment facilities, variation in flow or pollutant load, or changes in the influent stream. To allow for this variability, performance standards must necessarily be set above the plant's long-term average performance. However, effluent limitations guidelines must be set at a level low enough to ensure adequate control. Establishing effluent guidelines that balance these factors means that occasional, infrequent instances of non-compliance are statistically predictable at well-operated and maintained treatment facilties. Since pollutant discharge is often expressed in terms of average level, it is convenient to describe standards of performance and allow variability in terms of multiples of this average. Such a method of computing standards as functions of multiples of average level performance is explained below. The ratio of the pollutant standard level to the estimated long-term average is commonly called the "variability factor".

This factor is especially useful with lognormally distributed pollutant levels because its value is independent of the long-term average, depending only upon the day-to-day variability of the process and the expected number of excessive discharge periods. For a lognormal population, the variability factor (P/A), the performance standard P, and the long-term average A, are related by:

$$\ln(P/A) = S'(Z - S'/2)$$

where

A. "ln" represents the natural logarithm (base e) of a numerical quantity.

B. S' is the estimated standard deviation of the logarithms of pollutant level measurements. In the calculations which follow, S' is computed by the statistical procedure known as the "method of moments". The "method of moments" is a commonly used method of estimating the parameters of a population distribution from computed characteristics of the sample distribution. In this case, the mean and variance (the first two "moments") of the lognormal distribution were equated to the mean and variance of the sample distribution. The formula for the parameter, S', was then derived (S' is the standard deviation of the logarithms).

C. Z is a factor derived from the standard normal distribution. Z is chosen to give performance limitations which provide a balance between appropriate consideration of day to day variation in a properly operating plant and the necessity to ensure that a plant is functioning properly.

The value of Z used for determining performance standards for daily measurements of pollutant concentration is chosen as Z=2.33. This Z-value corresponds to the 99th percentile of the lognormal distribution meaning that only 1 percent of the pollutant observations taken from a plant with proper operation of treatment facilities would be greater than the performance standard, P. Use of this percentile statistically predicts one incident of non-compliance for every 100 samples for a plant in normal operation. Many plants in this industry are required by their NPDES Permits to self-monitor once per week. At this frequency, there will be 260 samples analyzed over the 5 year life of the permit. The use of the 99th percentile to establish daily maximum limitations statistically predicts 2 to 3 incidents of non-compliance per pollutant in 5 years. This percentile has been used to establish daily maximum limitations for inorganic chemicals manufacturing.

A. Calculation of Variability Factors

As mentioned above, development of variability factors for daily pollution level measurements was based on the assumption that these data, $(X1, X2, \ldots Xn)$, follow a lognormal distribution. When this distribution is not a precise model, lognormally based procedures tend to somewhat overestimate variability and produce liberal standards which act to the benefit of permittees.

Following this assumption, if $Yi = \ln(Xi)$, where $\ln(Xi)$ represents the natural logarithm or log base e of the pollution measurement, then the Yi; $i = 1, 2, \ldots, n$ are each normally distributed. If A' and S' are the mean and standard deviation of $Y = \ln(X)$ respectively, then the probability is k percent that an individual Y will not exceed $A' + ZS'$, where Z is the k-th percentile of the standard normal distribution, e.g., $Z = 2.33$ is the 99th percentile of the standard normal distribution. It follows that $A' + ZS'$ is the natural logarithm of the k-th percentile of X and that the probability is k percent that X will not exceed a performance standard $P = \exp(A' + ZS')$. The variability factor VF, is obtained by dividing P by A. For the lognormal distribution, the best measure of central tendency, or the expected value, is $A = \exp(A' + S'(S'/2))$. Hence,

$$VF = \frac{P}{A} = \frac{\exp\ (A' + ZS')}{\exp\ (A' + S'\ (S'/2))}$$

$$= \exp\ [A' + ZS' - (A' + S'\ (S'/2))]$$

$$= \exp\ [ZS' - S'\ (S'/2)]$$

$$= \exp\ [S'\ (Z - S'/2)]$$

$$\ln(VF) = \ln(P/A) = S'(Z - S'/2)$$

To estimate the VF for a particular set of monitoring data, where the method of moments is used, S' is calculated as the square root of $\ln(1.0 + (CV)^2)$, where the sample coefficient of variation, $(CV = S/X)$, is the ratio of sample standard deviation to sample average. The performance standard is then calculated by multiplying the variability factor, VF, by the long-term average, A. In these calculations, the sample average, X, is used as the unbiased estimator of A (the best estimate of A)(22).

B. Example Calculation of Variability Factors From Long-Term Data

Given the following descriptive statistics for a particular parameter, as might be found for zinc (mg/l)in Appendix A:

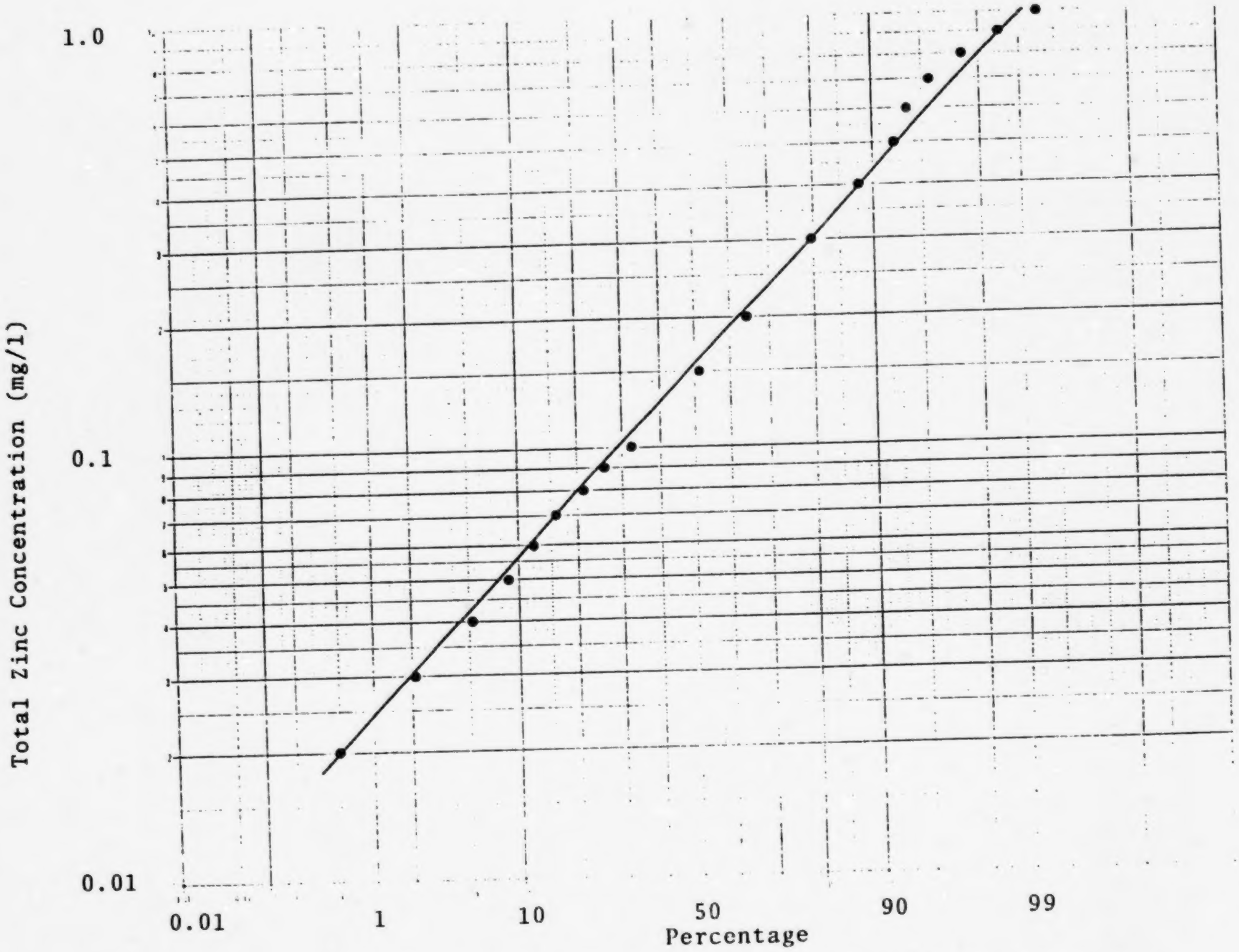

Figure 8-1 Cumulative distribution of daily concentrations of zinc (total) in treated effluent (59 months).

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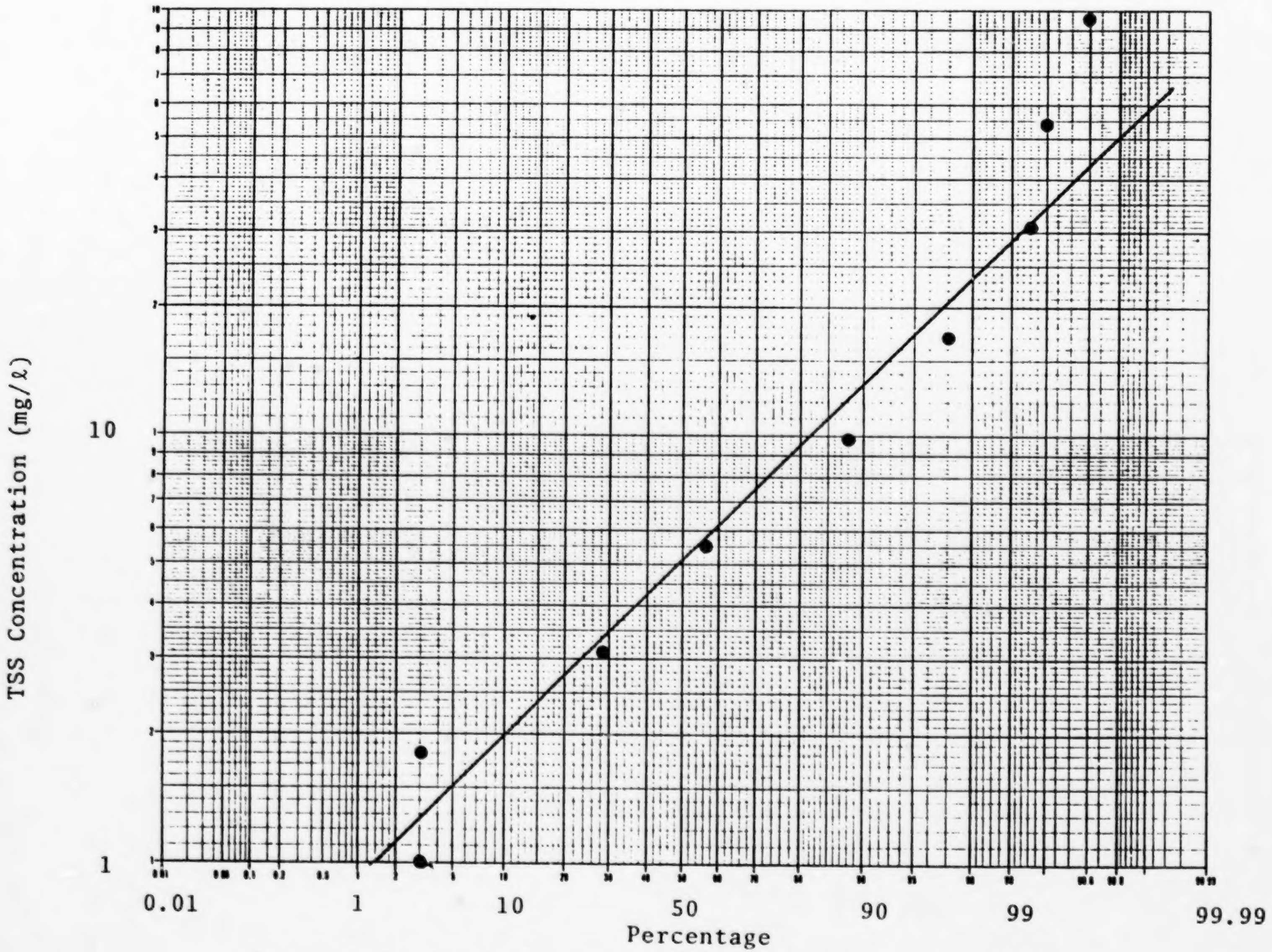
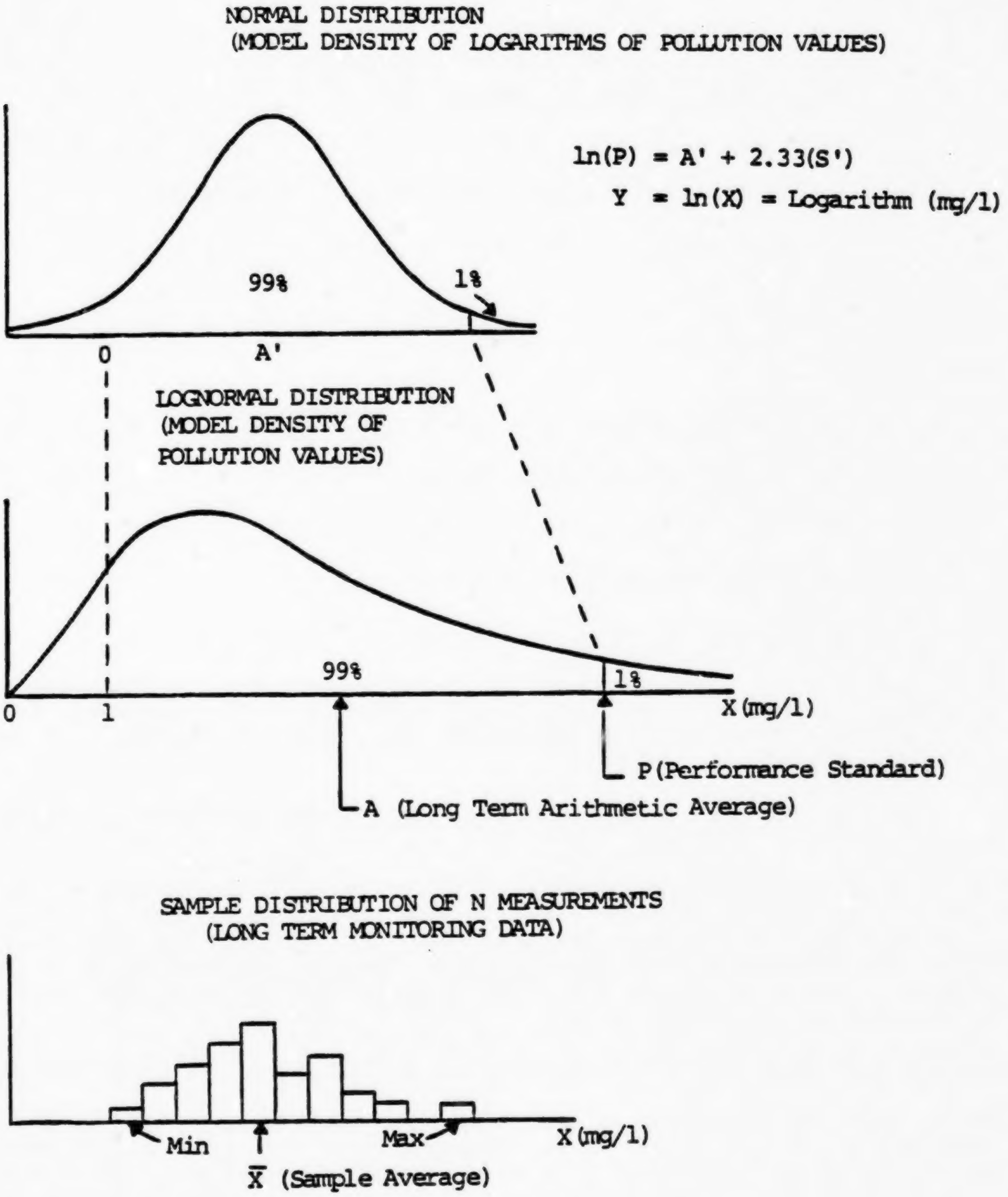


Figure 8-2. Cumulative distribution of daily concentrations of TSS in treated effluent over a 71 month period.



Note: (a) S' is estimated as $(S')^2 = [\ln(1 + CV^2)]$

$CV = S/\bar{X}$

$S^2 = \Sigma\ (X-\bar{X})^2/(N-1)$

$\bar{X} = \Sigma X/N$

Figure 8-3. Statistical distribution for daily pollution measurements.

No	Min	Avg	Max	CV
442	0.014	0.224	4.4	1.26

Calculate the estimated standard deviation of logarithms

$$(S')^2 = \ln(1.0 + (1.26)^2) = 0.951$$

$$S' = 0.975$$

Then:

$$\ln(P/A) = 0.975(2.33 - 0.975/2) = 1.796$$

The variability factor VF is,

$$VF = P/A = \exp(1.796) = 6.03$$

The performance standard P;

$$P = A(VF) = A\ (P/A) = (0.224)\ (6.03) = 1.35$$

That is, using the descriptive statistics for a pollutant presented above and the statistical approach just described, the daily maximum limitation established for that pollutant in a guideline would be 1.35 mg/l.

The statistical distributions relevant for the analysis of daily data are shown in Figure 8-3.

The statistical interpretation of P, the performance standard, is that one estimates that 99 percent (for the selected $Z=2.33$ value corresponding to the 99th percentile) of the daily pollution level measurements will not exceed P. For large data sets, P is roughly equivalent to an upper 99 percent confidence bound for an individual daily measurement.

Assumptions Concerning 30-day Average Pollutant Level Observation

While individual pollution level measurements should be assumed lognormally distributed, that assumption is not appropriate when analyzing 30-day averages. These averages generally are not distributed as lognormal quantities. However, for averages of daily (lognormal) measurements, a statistical principle, the "Central Limit Theorem", provides the basis for using the normal probability model. Therefore, the methods used in computing historical performance characteristics for 30-day averages differ from those used for daily samples. In this case, the sample coefficient of variation is the primary determinant of the variability factor, and there is no need to resort to logarithmic transformation. Examples of the propriety of this assumption is the cumulative distribution of 30-day averages shown in Figures 8-4 and 8-5. A straight line plot here on normal probability paper indicates the validity of this model.

Under these conditions, the 30-day average values (X^1, X^2, ... Xm), for m months behave approximately as random data from a normal distribution with mean A and standard deviation S". Therefore, the probability is k percent that a monthly average X will not exceed the performance standard P, where

$$P = A + Z(S")$$

The variability factor is:

$VF = P/A = 1.0 + Z(S"/A)$ and will be estimated by

$$VF = 1.0 + Z(CV)$$

Where:

1. Z is a factor derived from the standard normal distribution. If one wishes a performance standard based upon expecting 95 percent of monthly averages to be within guidelines, then Z=1.64 should be used.

2. CV is the estimated coefficient of variation of the 30-day averages and is computed by Sx/X, the ratio of standard error of sample means to overall or grand average of monthly averages.

Calculation of Variability Factors

A sample calculation of 30-day average variability factor is shown below. The descriptive statistical data is for lead (mg/l) from Appendix A:

No	Min	Avg	Max	CV
38	0.025	0.036	0.047	0.15

$$VF = 1 + Z(CV) = 1.0 + 1.64(0.15) = 1.25$$

$$P = A(VF) = (0.036)(1.25) = 0.045$$

That is, the maximum 30-day average effluent limitation derived from the descriptive statistics above would be 0.045 mg/l for that pollutant.

Given the previous descriptive statistics for a particular sample, one obtains the performance standard P, by multiplying the mean of the 30-day averages in the data set by VF. An appropriate statistical interpretation is that, for the selected value of Z=1.64 corresponding to the 95th percentile of a normal distribution, one estimates that 95 percent of the 30-day average pollution level measurements will not exceed P, or in other words, the statistics predict an average of 3 incidents of non-compliance with the 30-day average per pollutant over the 5-year (60-month) life of a permit at a well-operated and maintained treatment facility. This is essentially the same number of predicted incidents of non-compliance as was predicted for daily maximum limitations derived using the 99th percentile confidence level (see above). In Phase I, the 95th percentile confidence level was used to establish the 30-day average limitations. Moreover, in a number of instances, plants in Phase II also make Phase I chemicals and treat the wastewater in the same treatment facility.

In developing the statistical derivatives for monthly averages, in many cases, a full 30 days of daily average determinations were not available. In the above example, the monthly average is based on eight data points taken during the month. The standard deviation is then derived from these "monthly" averages assuming a normal distribution for the population of averages. Permits are usually written on the basis of monthly averages obtained from fewer than 30 data points per month. The use of such "monthly" averages results in a higher variability than averages based on 30 data points per month and, hence, a less stringent performance standard than would be attained using 30-day averages based on 30 data points per month.

Figure 8-6 shows the relationship between the normal probability model and frequency distribution of a set of 30-day averages.

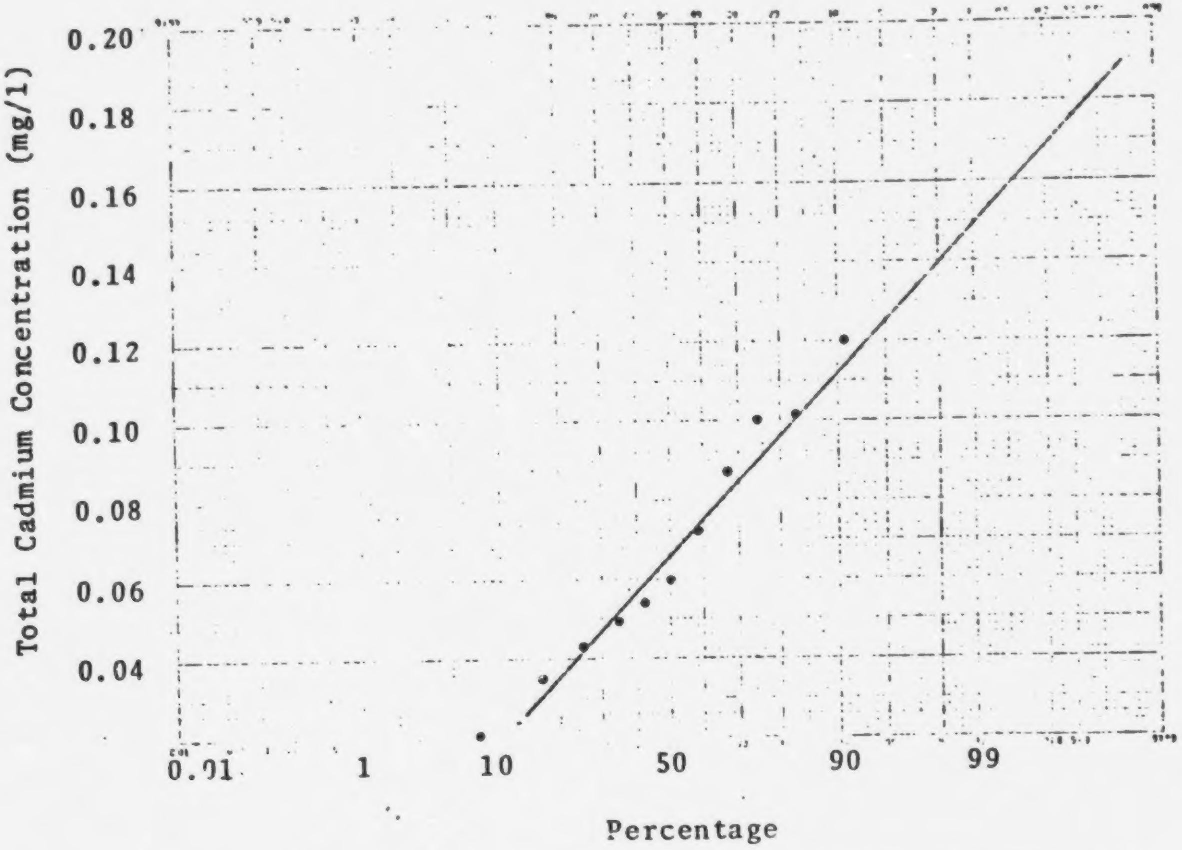


Figure 8-4. Cumulative distribution of monthly averages of cadmium in treated effluent (24 months).

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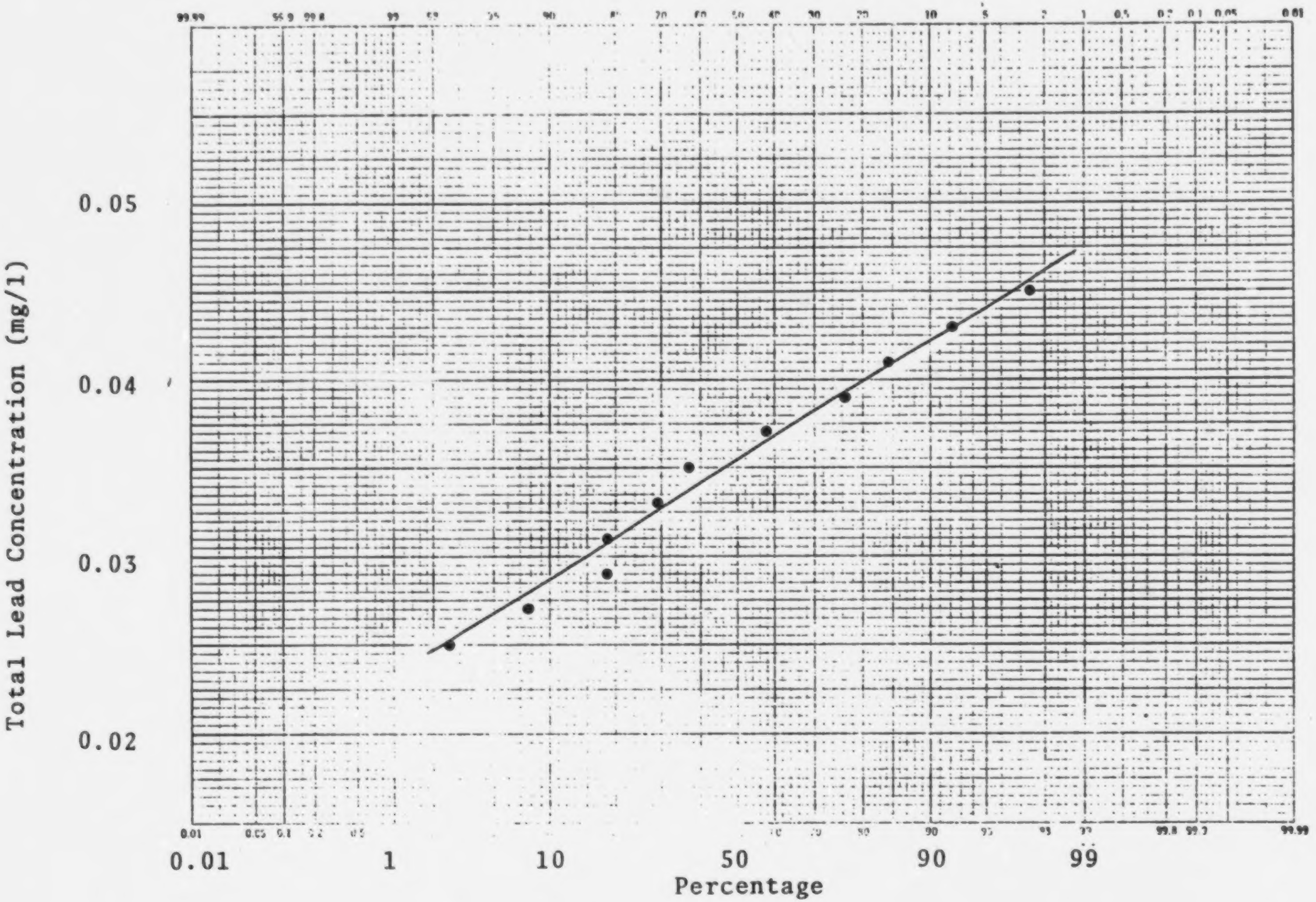

Figure 8-5 Cumulative distribution of monthly averages of lead (total) concentrations in treated effluent (intermittently for 38 months).

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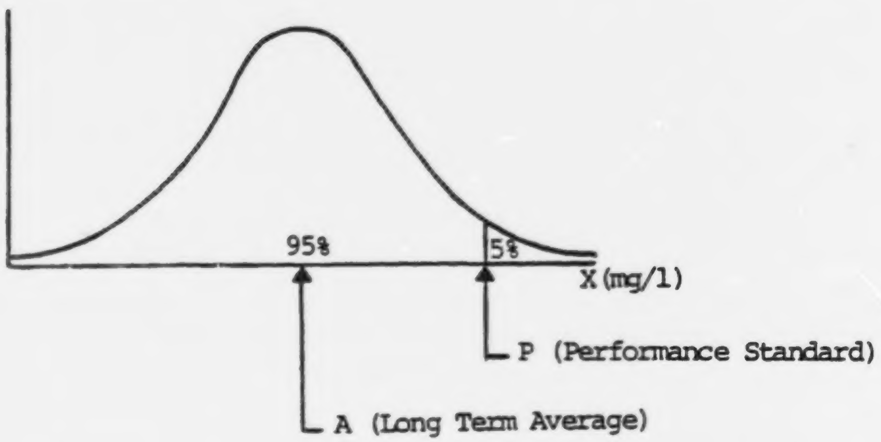
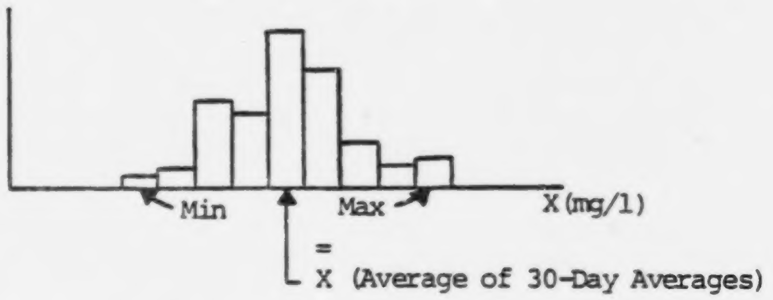
NORMAL DISTRIBUTION
(MODEL DENSITY OF 30-DAY AVERAGE POLLUTION MEASUREMENTS)



SAMPLE DISTRIBUTION OF M MONTHLY AVERAGES
(LONG TERM MONITORING DATA)



Note: (a) $P/A = 1+1.64\,(CV)$

$$CV = S_{\bar{X}} / \bar{\bar{X}}$$

$$(S_{\bar{X}})^2 = (\Sigma\ (\bar{X}-\bar{\bar{X}}) / (M-1))$$

$$\bar{\bar{X}} = \Sigma\ \bar{X}/M$$

Figure 8-6. Statistical distributions for 30-day average pollution measurements.

SECTION 8

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SECTION 9

TREATMENT TECHNOLOGY APPLICATIONS FOR TOXIC POLLUTANT REMOVAL

Selection of Pollutants to be Controlled

In order to determine which toxic pollutants, if any, may require effluent limitations, the pollutants observed in each subcategory were evaluated with regard to their treatability on the basis of the raw waste concentrations found during screening and verification. In an attempt to determine the need for regulation the toxic metals were divided into two groups:

Group 1 - Those priority pollutants which appear at concentration levels that are readily treatable using available technology.

Group 2 - Other treatable and/or potentially treatable priority pollutants observed in the subcategory. These include toxic metals which exist at concentrations below the minimum treatability limit and above the minimum detection level. The Group 2 pollutants would be controlled by the same treatment technology used to control the Group 1 pollutants.

Table 9-1 presents the significant toxic pollutant metals found in each group. In general, those metals occurring in the first group are of prime concern and require regulation, while those occurring in the second group are of somewhat less concern and are not expected to require regulation. Metals in Group 2 are controlled by the technologies used to control the metals in Group 1, which are the dominant metals in the raw wastewater and are directly related to the particular product, process involved, or raw material.

Application of Advance Level Treatment and Control Alternatives

General Design Objectives

Beginning with Section 11 of this document, the selection and application of toxic pollutant treatment and control technology for model plant systems for each of the regulated subcategories are described. Several levels of treatment are indicated. Level 1 represents existing treatment systems and the advanced level (Level 2) is the selected technology for step-wise improvements in toxic pollutant removal over that achieved by the Level 1 system. Flow diagrams show Level 1 components as a starting point for advanced level treatment additions and incremental cost estimates.

TABLE 9-1. Listing of priority and non-conventional pollutants recommended for consideration by subcategory

Subcategory	Group 1(1)	Group 2(2)
Cadmium Pigments and Salts	Cadmium Selenium Zinc	Antimony Arsenic Barium Chromium Copper Lead Nickel
Cobalt Salts	Cobalt Copper Nickel	Lead Zinc
Copper Salts	Copper Nickel	Antimony Arsenic Chromium Lead Zinc
Nickel Salts	Nickel Copper	Antimony Cadmium Chromium Lead Zinc
Sodium Chlorate	Chromium (Total) Chlorine (Total Res.)	Antimony Copper Lead Nickel Zinc Chromium (VI)
Zinc Chloride	Arsenic Zinc	Antimony Cadmium Chromium Copper Lead Nickel Silver

---

(1) Group 1 - dominant raw waste pollutants as control parameters for effluent limitations or guidance.

(2) Group 2 - secondary raw waste pollutants found less frequently and at lower concentrations. These pollutants have not been selected as control parameters but are expected to receive adequate treatment as a result of controlling the Group 1 pollutants.

For both existing and new sources, the advanced level technology options are selected as candidates for BAT with toxic pollutant removal as the primary objective. Although the advanced level systems chosen also give improved performance over the Level 1 systems for the removal of conventional and nonconventional pollutants, this is regarded as a secondary design objective.

Pretreatment Technology

Since untreated heavy metal ions will either pass through the treatment provided in a typical POTW, or will be precipitated with the POTW solid residue, pretreatment of wastes containing significant amounts of heavy metals is necessary. As a general rule, alkaline precipitation, followed by settling and removal of the solids will suffice. Normally the Level 1 or 2 model treatment processes shown in the following subsections will be appropriate for pretreatment prior to discharge to a POTW. Pass-through would occur in the absence of pretreatment when BPT or BAT treatment would reduce toxic metal concentrations by a greater percent than is achieved by a POTW.

New Source Performance Standards

New Source Performance Standards are at least equal to BAT. In cases where new plants have the opportunity to design systems for better toxic removal performance without expensive retrofitting, EPA has used the higher technology systems as a basis for regulation.

Estimated Achievable Performance Characteristics for Advanced Level Applications

Advanced level control and treatment alternatives for reduction of pollutant discharges and their applicability to each subcategory are presented in the sections dealing with individual products. With few exceptions, these alternatives were selected specifically for removal of priority pollutants and were designed for end-of-pipe treatment.

Treatment technologies practiced outside the industry are recommended when appropriate and, in most cases, apply to the removal of toxic pollutant metals. The estimated long-term average treatability levels (Section 8, Tables 8-11, 8-12, 8-13), long-term data parameters, and the screening and verification results are all utilized in the development of estimated performance characteristics for the indicated treatment applications in each subcategory.

Advanced Level Removal of BPT Pollutants

Performance estimates for these systems, when possible, were based on effluent quality achieved at plants currently practicing these technologies. However, in some cases, the advanced levels are not currently being practiced within the specific subcategory of concern, and performance information from other appropriate sources is necessarily utilized.

When established wastewater treatment practices, such as clarification or filtration, form a part of advanced treatment alternatives, the specified achievable effluent quality has been based on concentrations accepted as achievable through proper design and control. The prime example of this is suspended solids reduction by filtration.

Advanced Level Removal of Toxic Pollutants

Performance estimates for toxic pollutants were also based, when possible, on effluent quality achieved at plants currently practicing these technologies. However, in some subcategories, toxic pollutant analyses are not conducted unless a specific pollutant is regulated and requires monitoring. Where transfer of technology is applied as a treatment alternative, performance estimates for toxic pollutant removals were based on the demonstrated performances in other industries while incorporating allowances for specific differences in process waste characteristics and operating conditions. Statistically derived long-term monitoring data parameters were described in Section 8 and are compiled in tabular form in Appendix A. The sampling data are used to supplement the available long-term data applied to each subcategory. A judgment is made whether the sampling data represent a well-performing system or one which is not performing at its technological potential. For a well-performing system, the sampling data are regarded as representative of long-term averages and are compared with the estimated treatability ranges from Table 8-11, as well as the long-term averages developed from long-term data. In this manner, the performance estimates for each pollutant, at each treatment level for the subcategories, are developed and presented in tabular summaries. By starting with the estimated achievable long-term averages, the specific variability factors derived for each pollutant are used to estimate the daily maximum values and 30-day average values.

Pollution Control Parameters to be Regulated

Conventional Pollutants

Wastewater quality parameters which are identified as conventional pollutants include the following:

pH
Total Suspended Solids (TSS)
Biochemical Oxygen Demand, 5-Day (BOD-5)
Fecal Coliform
Oil and Grease

Only the first two parameters (pH and TSS) in this group have been selected for regulation in the Inorganic Chemicals Manufacturing Point Source Category, because the other three pollutants are not found at treatable levels in inorganic chemical process wastewaters, and are not associated with inorganic chemical manufacturing. For direct dischargers, the pH range of 6 to 9 (6-10 in the zinc chloride subcategory) has been established as the general control limitation. For continuous monitoring of pH, 40 CFR §401.17 allows pH excursions of up to one hour per day. The limitations on TSS are specified for both BPT and BCT-based regulations, the former being largely a function of industry performance and the latter stemming from treatability estimates with the appropriate technologies.

Nonconventional Pollutants

The wastewater quality parameters classified as nonconventional pollutants include the nontoxic metals such as aluminum, boron, barium, cobalt, and iron along with chemical oxygen demand (COD), total residual chlorine, fluoride, ammonia, nitrate, and "phenols," etc. Of these, only total residual chlorine and cobalt were considered for regulation in this group of the inorganic chemicals industry because they were the only nonconventional pollutants detected at treatable levels. Due to its toxicity, chlorine would be controlled in direct discharges, but would be excluded from control in pretreatment regulations because influent to POTW's is often chlorinated.

Toxic Pollutants

The toxic pollutants found at significant levels during screening and verification are listed by subcategory in Table 9-1. Of these, toxic pollutant control parameters were selected largely on the basis of treatability. Since several toxic pollutants may be controlled by a common treatment technology, it is possible to select one or more control parameters which will act as a surrogate for others exhibiting the same treatability characteristics. Treatment system operating conditions would normally be optimized for the removal of the specified control parameters which would be monitored on a regular basis. The other toxic pollutants would be monitored much less frequently as a periodic check of the effectiveness of surrogate control.

The following toxic metals and nonconventional pollutants have been designated as control parameters in this point source category:

Antimony
Arsenic
Cadmium
Cobalt
Chlorine (Total Residual)
Chromium (Total)
Copper
Lead
Nickel
Selenium
Zinc

The specific control parameters selected for each subcategory are presented in the tables entitled "Control Parameter Limitations" in the sections of this report dealing with the individual industries. Some general comments about them are given here.

The most common technology applied in industry for the removal of chromium from wastewaters involves a reduction step, whereby Cr (VI) in solution is converted to the less toxic Cr (III) form which can then be removed by alkaline precipitation. The efficiency of this treatment depends upon the presence of an excess reducing agent and pH control to drive the reduction step to completion. When treated effluent samples are collected to monitor residual Cr (VI) and total chromium levels, the analytical results for Cr (VI) are subject to several factors which adversely affect the accuracy and reproducibility of the diphenylcarbazide (DPC) colorometric method. The problem is not so much one of analytical interferences with the Cr (VI) - DPC color development, but rather the actual changes in Cr (VI) concentration that can take place during sampling, sample preservation and storage, and analysis. The major cause of such changes is the presence of an excess reducing agent in the treated effluent. This tends to give false low readings for Cr (VI) although in some cases the opposite may occur as a result of sample preservation and storage under acidic oxidizing conditions.

Thus, in view of the questionable reliability of the presently accepted Cr (VI) monitoring procedure, total chromium, Cr (T), is recommended as the control parameter to be used in the inorganic chemicals industry. The adequacy of Cr (T) as a control parameter is predicated on its effectiveness as a surrogate for Cr (VI) control. Since the concentration of Cr (T) represents the summation of all forms of chromium normally found in solution or suspension including Cr (VI), the final concentration of Cr (T) in a treated effluent is dependent on the effectiveness of both the reduction and the alkaline precipitation steps. In this way, the use of Cr (T) as the control parameter assures that adequate removal of Cr (VI) is being achieved as a direct consequence of the treatment technology required.

SECTION 10

COST OF TREATMENT AND CONTROL SYSTEMS

INTRODUCTION

The costs, cost factors, and costing methodology used to derive the capital and annual costs of treatment and control systems are documented in this section. All costs are expressed in 3rd quarter 1982 dollars.

The following categorization is used for presenting the costs:

Capital Costs

Facilities
Equipment (including monitoring instrumentation)
Installation
Engineering
Contractor Overhead & Profit
Contingency
Land

Annual Costs

Operations and Maintenance
Operating Personnel
Facility and Equipment Repair and Maintenance
Materials
Energy
Residual Waste Disposal
Monitoring, Analysis and Reporting
Taxes and Insurance
Amortization

TREATMENT AND DISPOSAL RATIONALE

The following assumptions are employed in the cost development:

A. Noncontact cooling water generally is excluded from treatment (and treatment costs) provided that no pollutants are introduced.

B. Water treatment, cooling tower and boiler blowdown discharges are not considered process wastewater unless such flows contain significant amounts of pollutants.

C. Sanitary sewage flow is excluded.

D. Sodium chorate plants are assumed to operate 350 days a year, sodium chloride and sodium sulfite plants 365 days per year, and all other plants 250 days per year. All plants are assumed to operate 24 hours per day.

E. Manufacturing plants are assumed to be single product plants.

F. The inorganic chemical industry extensively uses in-plant control techniques such as in-process abatement measures, housekeeping practices, and recycling of process wastewaters to recover valuable materials or use these materials as feed for other by-products. Segregation of uncontaminated cooling and other waters prior to treatment and/or disposal, and other similar measures can contribute to waste load reduction. The costs associated with these activities are not included in the cost estimates.

G. Excluded from the estimates are any costs associated with environmental permits, reports or hearings required by regulatory agencies.

COSTS REFERENCES AND RATIONALE

The cost information developed in this report represents engineering estimates. The basic cost information utilized was obtained from a variety of sources including building construction manuals and vendors of the various types of equipment utilized in the prescribed treatment and disposal systems (References 1, 2, 3, 4, 5, and 6).

Selected facility and treatment system engineering cost estimates were validated by comparing computed costs with actual costs incurred for the installation of such facilities and equipment by contractors and vendors.

CAPITAL COSTS

Facilities

Lagoons/Settling Ponds. The cost of constructing lagoons can vary widely, depending on local topographic and soil conditions.

The costs and required areas of lagoons and settling ponds are developed as a function of volume (capacity). It is assumed that lagoons and settling ponds are rectangular in shape, with the bottom length twice the bottom width. The dikes are constructed with a 2:1 slope and a 3m (10 ft.) top surface to permit sludge removal by the clamshell method. The interior area is excavated to a depth sufficient to provide all the material needed for the construction of the dikes. The earth is assumed to be fairly heavy and to contain stiff clay.

A common, transverse dike is provided to permit alternate dewatering for sludge removal.

The cost-estimating relationship shown below is used to estimate lagoon/settling pond costs.

1.1 ((\$0.25 x total area) + (\$5.15 x dike volume)
+ (\$0.45 x dike surface))

The 1.1 factor represents the cost of the common, transverse dike. The cost factors are derived from References 1 and 2. The cost factor applied to the total area occupied by the impoundment (measured in square meters) is for clearing with a bulldozer. The cost factor associated with dike volume (measured in cubic meters) includes excavation with a bulldozer, compaction and grading. The cost factor associated with the dike surface (measured in square meters) represents the cost of fine grading.

The variables required for the use of the cost-estimating relationship can be obtained from Figures 10-1, 10-2, 10-3.

Lagoons are unlined, except where specified. Liner material and costs are noted below:

Polyethylene (installed)	$\$6.50/m^2$ ($\$0.60/ft^2$)
Clay, 60 cm (2 ft) depth	
Clay on-site (installed)	$\$2.35/m^2$ ($\$0.20/ft^2$)
Clay off-site (installed)	$\$7.80/m^2$ ($\$0.70/ft^2$)

Perimeter fencing (chain link, industrial) is provided for lagoons and sludge disposal sites at a cost of \$8.80/linear meter (\$2.65/ft) plus a sliding gate at \$100.

Roads where necessary represent temporary (graded and graveled) roads 4 m (13 ft) in width. The cost is \$11/linear meter (\$3.30/ft).

Concrete Pits. Concrete pits are frequently used for the temporary storage of wastewater. Pit costs are shown in Figure 10-4a. The walls and floors of the pits are constructed of 20 cm (8 in) reinforced concrete. The costs are based on \$425 per cubic meter (\$327 per cubic yard) of reinforced concrete in place.

Buildings. Some equipment and material must be installed or stored in buildings. The building costs shown in Figure 10-4b represent the construction cost ($325 per square meter ($30 per square foot)) of warehouses and storage buildings. These cost estimates are based on Reference 2.

Piping. Pipe size requirements as a function of flow and piping costs (including an allowance for fittings) are shown in Table 10-1. Pipe costs are shown separately only where the wastewater must be transported outside the plant area, e.g., to lagoons or settling ponds. Piping used for the interconnection of equipment is included in the installation cost.

Equipment

Many of the described wastewater treatment and control systems consist of combinations of items such as chemical feed systems, mixers, clarifiers, filters, tanks, pumps, etc.

Parametric costs of these equipment items related to relevant variables are shown in Figures 10-5 to 10-9. Surface condenser costs for the sodium chloride subcategory are given in Section 17 - "BAT Revisions." The costs are bare equipment costs obtained from current catalogs, vendors and equipment manufacturers.

Other equipment costs employed include the following:

Hydrated Lime Storage and Feeder System	$40,000*
Pebble Lime Storage and Feeder System	$60,000*
Vacuum Filter (3' x 1')	$45,000
Vacuum Filter (3' x 3')	$55,000
Filter Cartridges	$100 - 300
Agitated Falling-Film Evaporator (316SS) 6 m^2**	$76,000
Agitated Falling-Film Evaporator (316SS) 7 m^2**	$85,000
Agitated Falling-Film Evaporator (316SS) 11 m^2**	$104,000
Multiple Effect Evaporator 9.3 m^2***	$100,000
Multiple Effect Evaporator 32.5 m^2***	$190,000

*For large-scale use of lime.
**Heat transfer area.
***Total heating surface.

Duplicate items are provided for critical items to permit continuous operation during equipment shutdown for scheduled and unscheduled maintenance.

It is assumed that monitoring equipment will be installed at the treated effluent discharge point. The basic monitoring requirements include the following:

1. pH measurement and recording
2. Flow measurement
3. Automatic sampling

The installed cost of this equipment is estimated to be $10,000.

Installation

Installation costs consist of material and labor. Material included piping, concrete, steel, instruments, electrical, insulation, paint and field materials. Labor includes direct and indirect costs for equipment erection and installation. These costs are extremely site-specific.

The factors shown below provide representative costs for types of systems considered in this report.

1. Installation materials	45% of bare equipment cost
2. Erection and installation labor	35% of equipment and installation material cost

They are based on Reference 3.

Engineering

This includes the design and inspection services to bring a project from a concept to an operating system. Such services broadly include laboratory and pilot plant work to establish design parameters, site surveys to fix elevations and formulate plant layout, foundation and groundwater investigations, and operating instructions; in addition to design plans, specifications and inspection during construction. These costs, which vary with job conditions, are often estimated as percentages of construction cost, with typical ranges as follows:

Preliminary survey and construction surveying	1 to 2%
Soils and groundwater investigation	1 to 2%
Laboratory and pilot process work	2 to 4%

Engineering design and specifications	7 to 12%
Inspection and engineering support during construction	2 to 3%
Operation and maintenance manual	1 to 2%

From these totals of 14 percent to 25 percent, a midvalue of 20 percent of in-place facility, equipment, and instrumentation costs has been used in this study to represent the engineering and design costs applied to model plant cost estimates. These costs include, in addition to the professional service hours, the costs for expenses such as telephone, reproductions, computer services, and travel.

Contractor Overhead and Profit

This cost is estimated as 15 percent of the installed plant cost (equipment, installation and engineering costs).

Contingency

This is an allowance of 10 percent applied to the total capital cost, excluding land, based on the status of engineering, design and specifications, quality of prices used, and the anticipated jobsite conditions. This covers design development (but not scope), errors and omissions, impact of late deliveries and unusually adverse weather conditions, variations in labor productivity and other unforeseen difficulties during construction.

The cost factors employed for engineering, contractor overhead and profit, and contingency correspond to those employed in Reference 4.

Land

Lagoons/settling ponds and sludge disposal areas can entail large land requirements. Land costs are included only where such facilities are prescribed.

The availability and cost of land can vary significantly, depending on plant location. For the purpose of this study, land is valued at $30,000/hectare or $12,000/acre.

ANNUAL COSTS

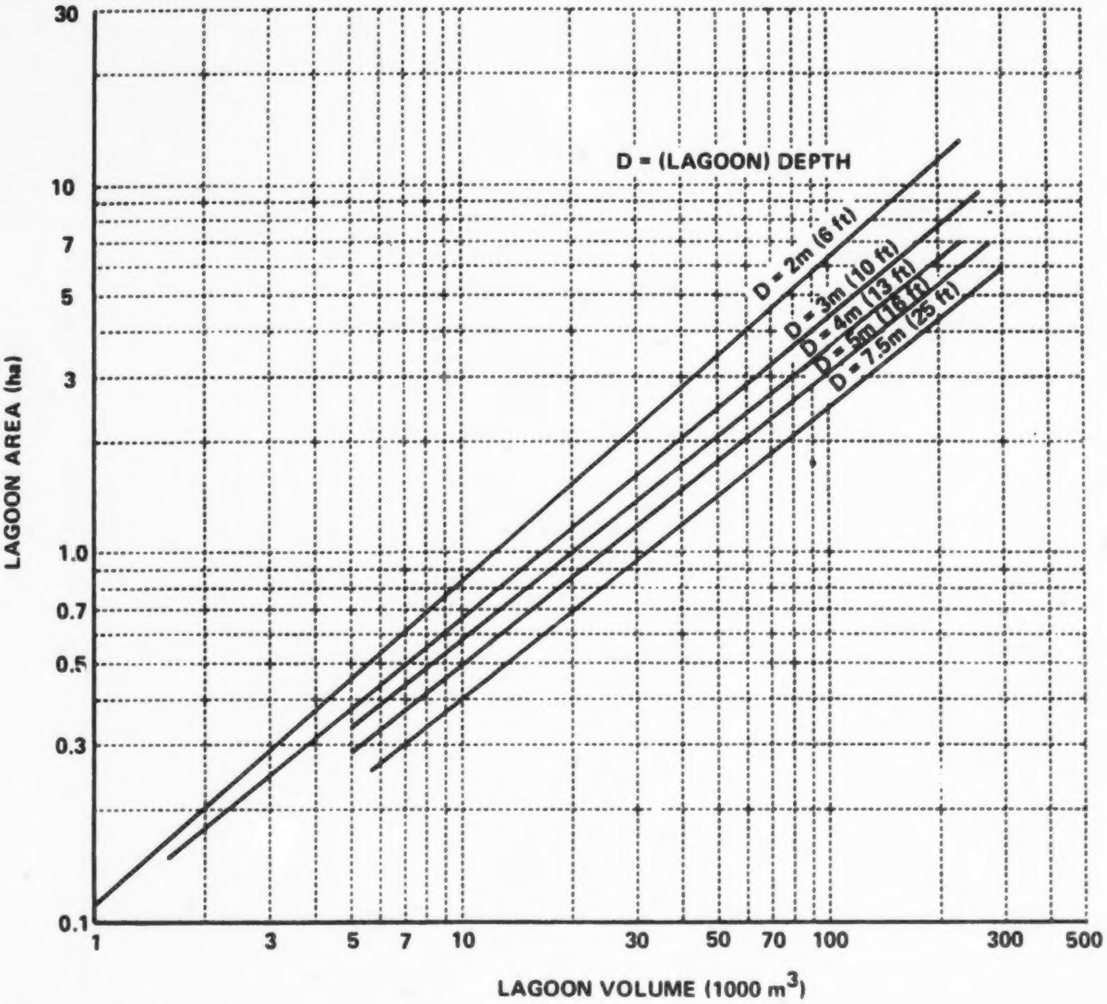
Operations and Maintenance

TABLE 10-1. PIPE SIZE REQUIREMENTS AND PIPE COSTS

DAILY FLOW			PIPE SIZE		PIPE COST*	
Cubic Meters	Cubic Meters/Min	Gal/ Min	CM	IN	$/LM	$/LF
100	0.07	18	2.5	1	44	13.50
150	0.10	27	5.0	2	48	14.60
350	0.24	64	7.5	3	59	18.10
650	0.45	119	10.0	4	72	22.00
2,500	1.74	458	15.2	6	109	33.00
4,500	3.13	824	20.3	8	167	51.00
8,000	5.56	1,468	25.4	10	220	67.10
12,500	8.68	2,292	30.5	12	280	85.40
35,000	24.31	6,418	45.7	18	470	143.30

*Installed above ground, includes allowance for fittings.

Figure 10-1. LAND REQUIREMENTS FOR SMALL AND MEDIUM LAGOONS



ha x 2.471 = acres

m^3 x 264.172 = gal

Figure 10-2. DIKE VOLUMES OF LAGOONS

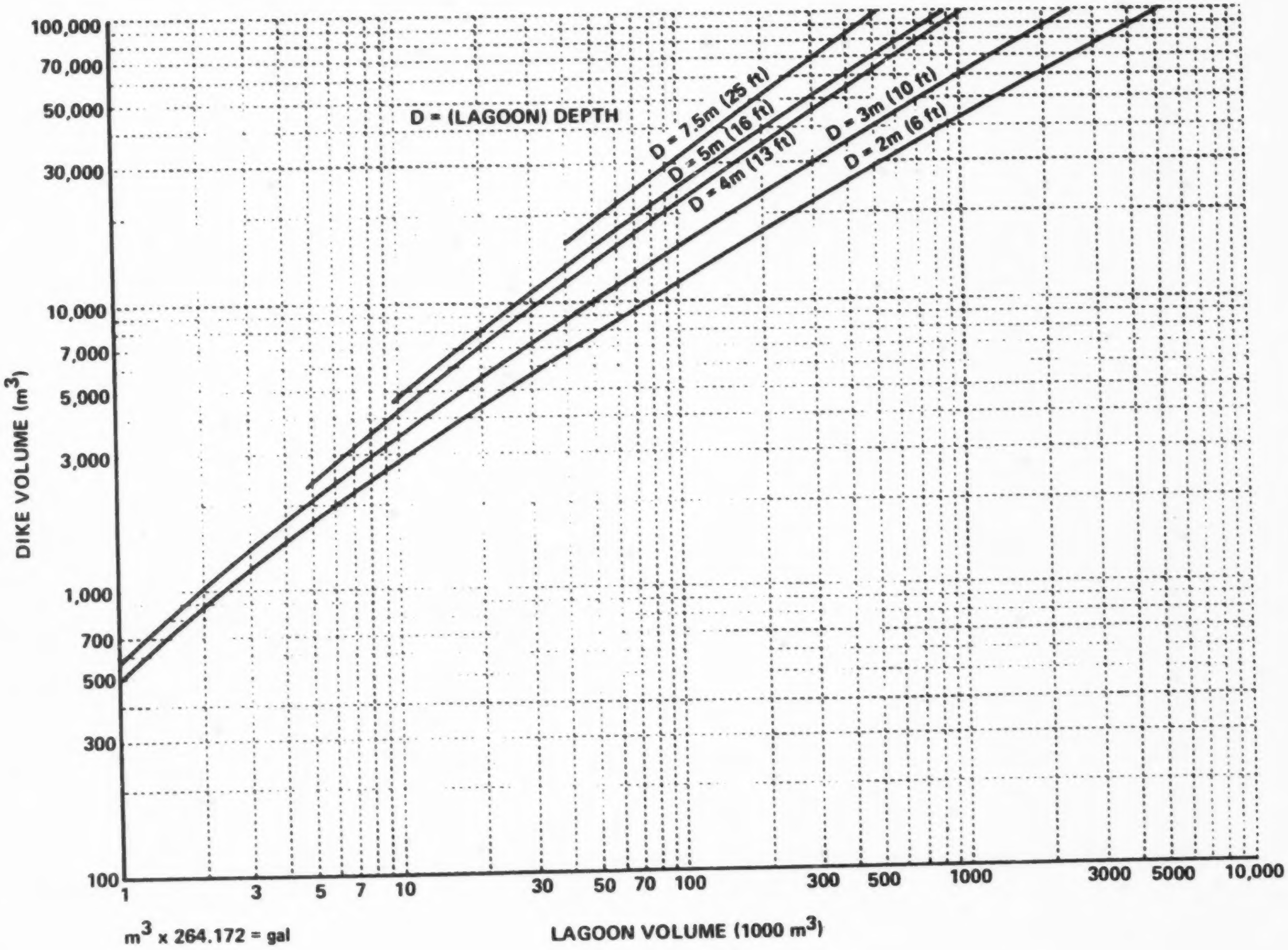
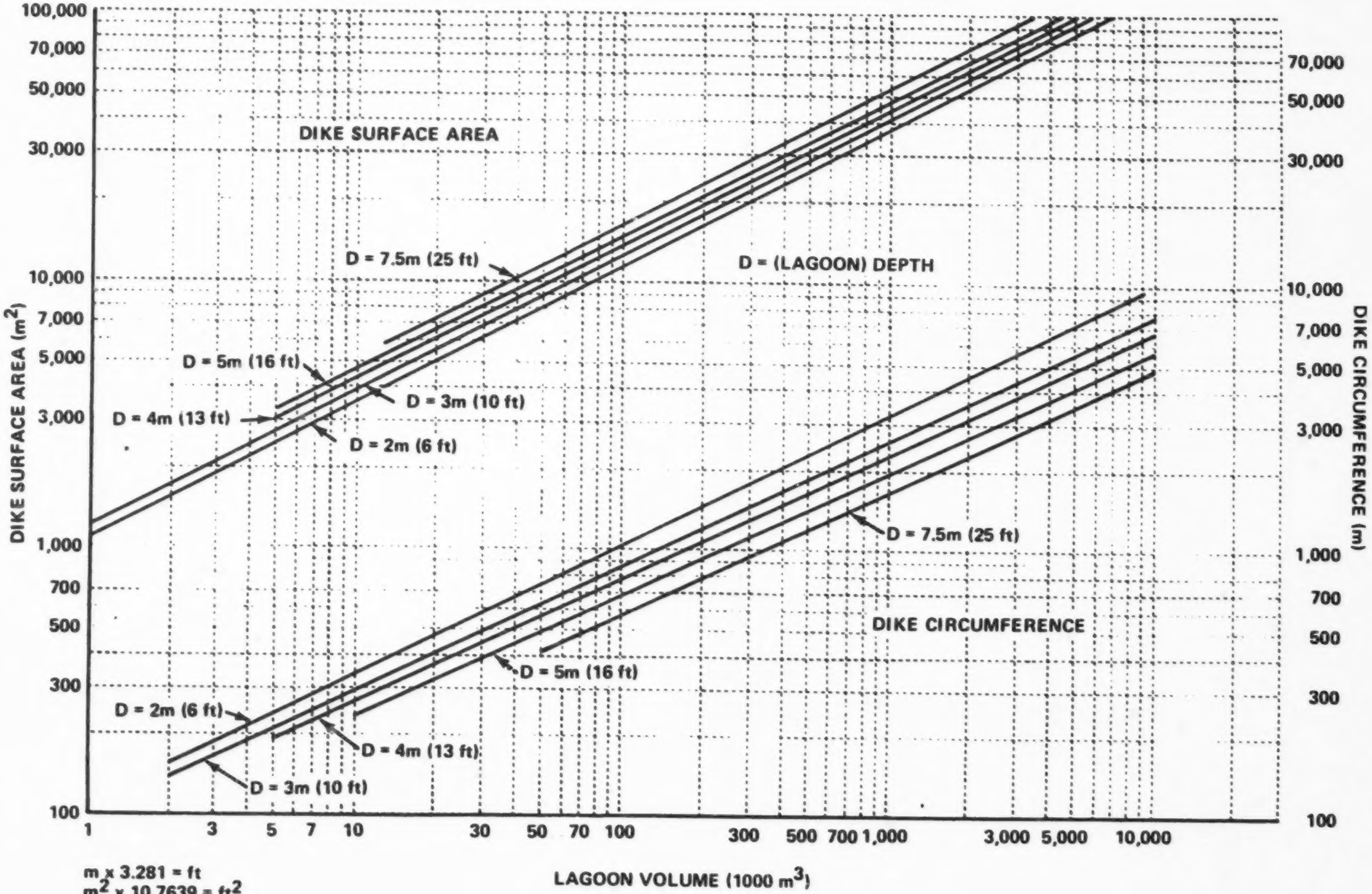
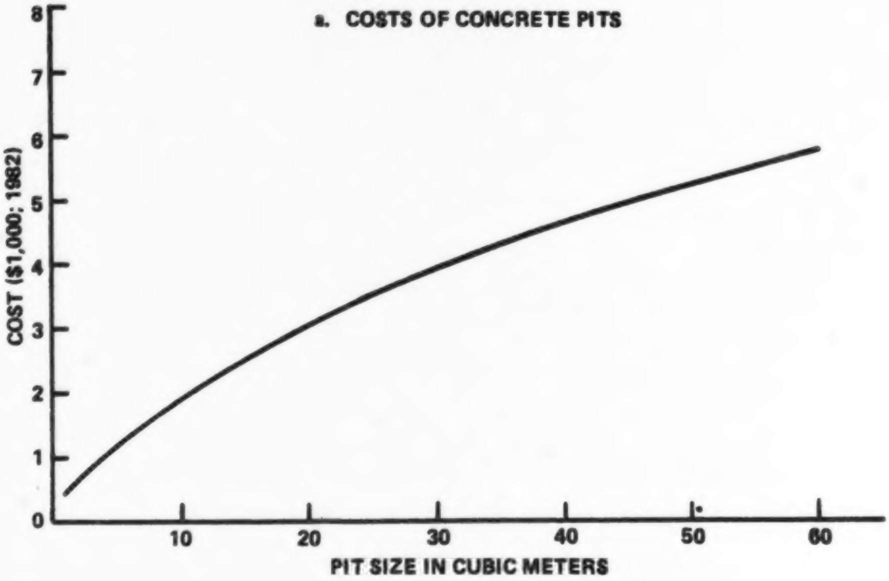


Figure 10-3. DIKE SURFACE AREAS AND CIRCUMFERENCES OF LAGOONS

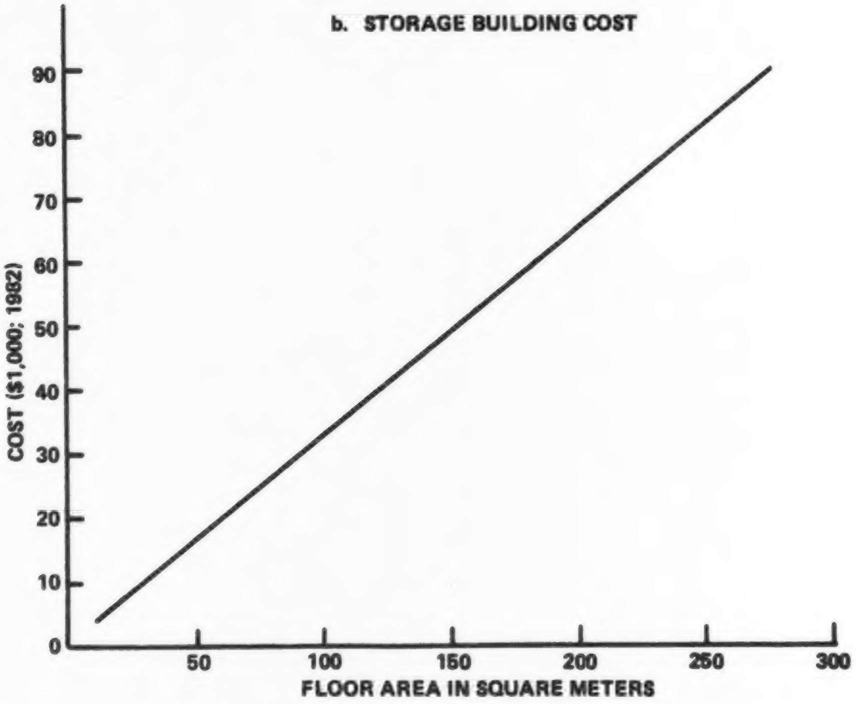


$m \times 3.281 = ft$
$m^2 \times 10.7639 = ft^2$
$m^3 \times 264.172 = gal$

Figure 10-4. CONCRETE PITS AND BUILDING COSTS



a. COSTS OF CONCRETE PITS



b. STORAGE BUILDING COST

Figure 10-5. HOLDING/STORAGE TANK COSTS

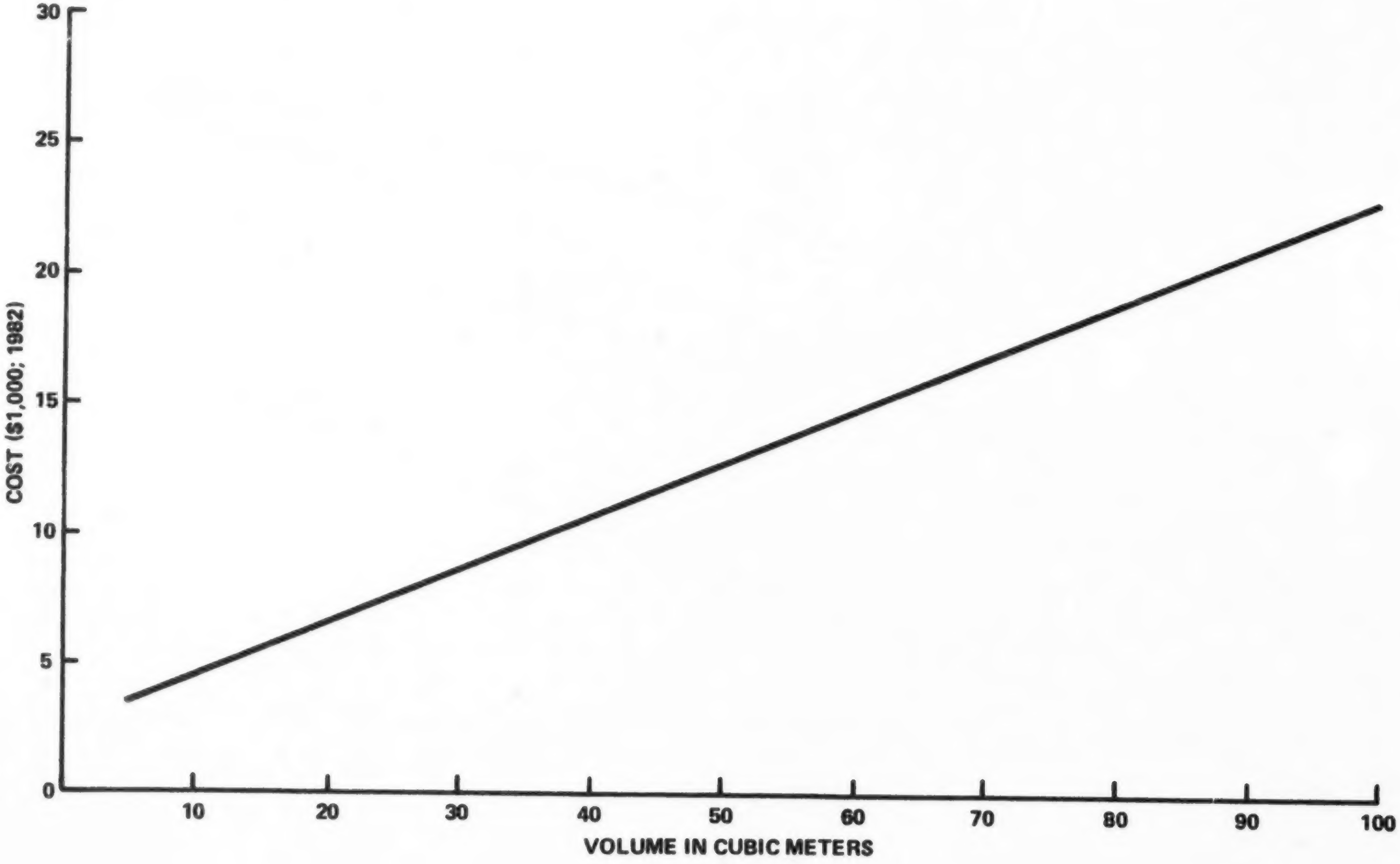


Figure 10-6. FILTER, THICKENER AND CLARIFIER COSTS

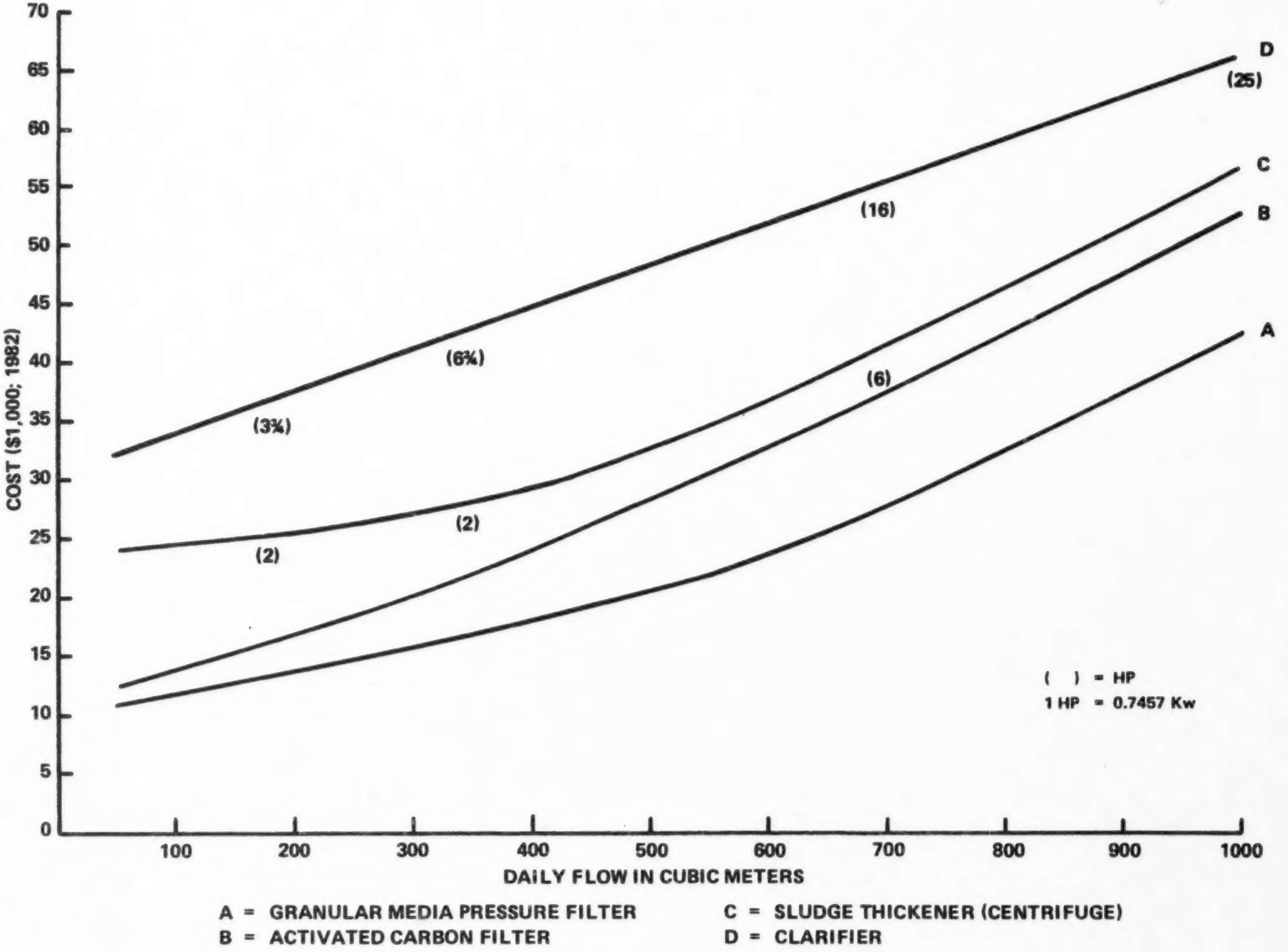


Figure 10-6b. GRANULAR MEDIA FILTRATION COST

(FLOW RATE = 290 l/m^2/min - 7 gal/ft^2/min)

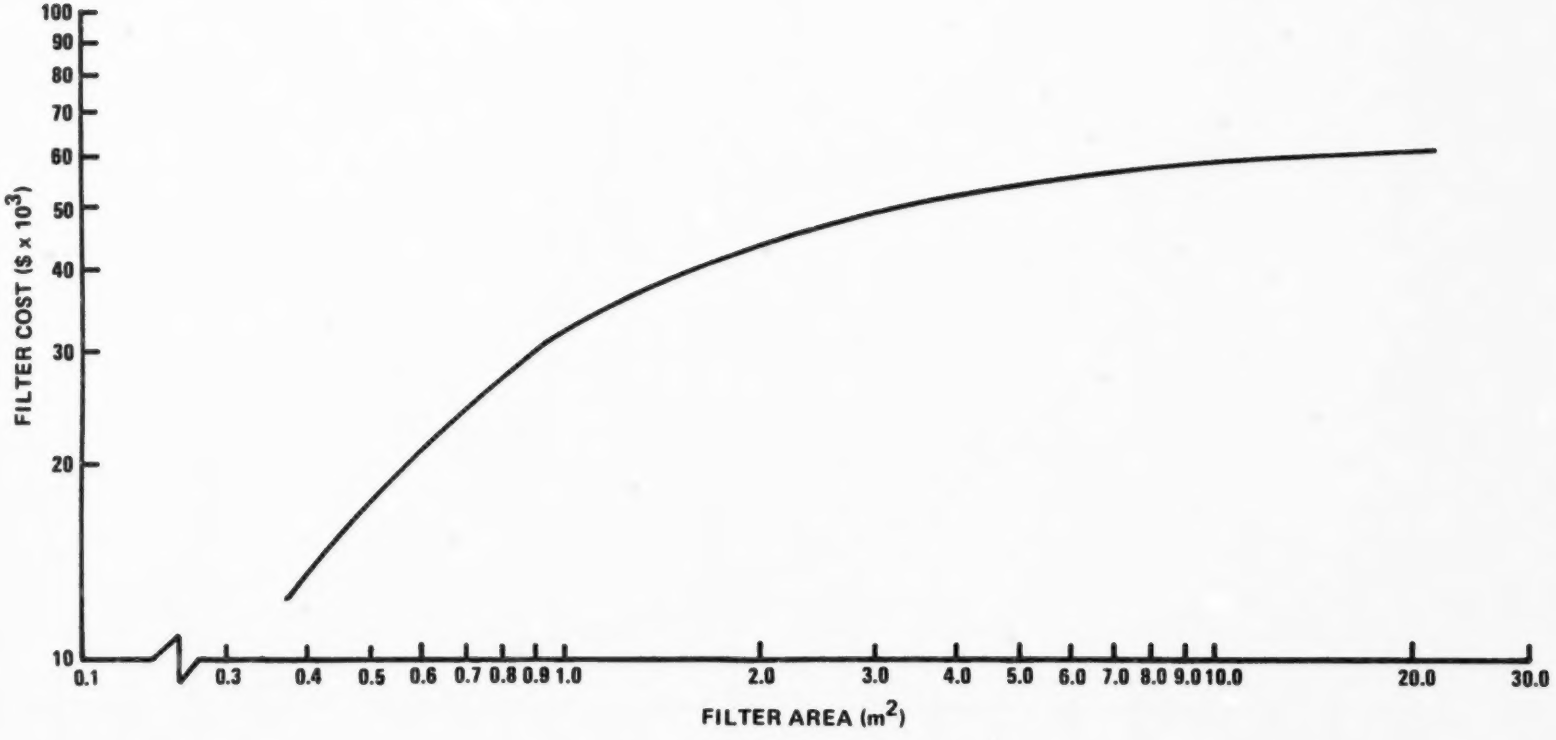


Figure 10-7. CHEMICAL FEED AND NEUTRALIZATION SYSTEM COSTS

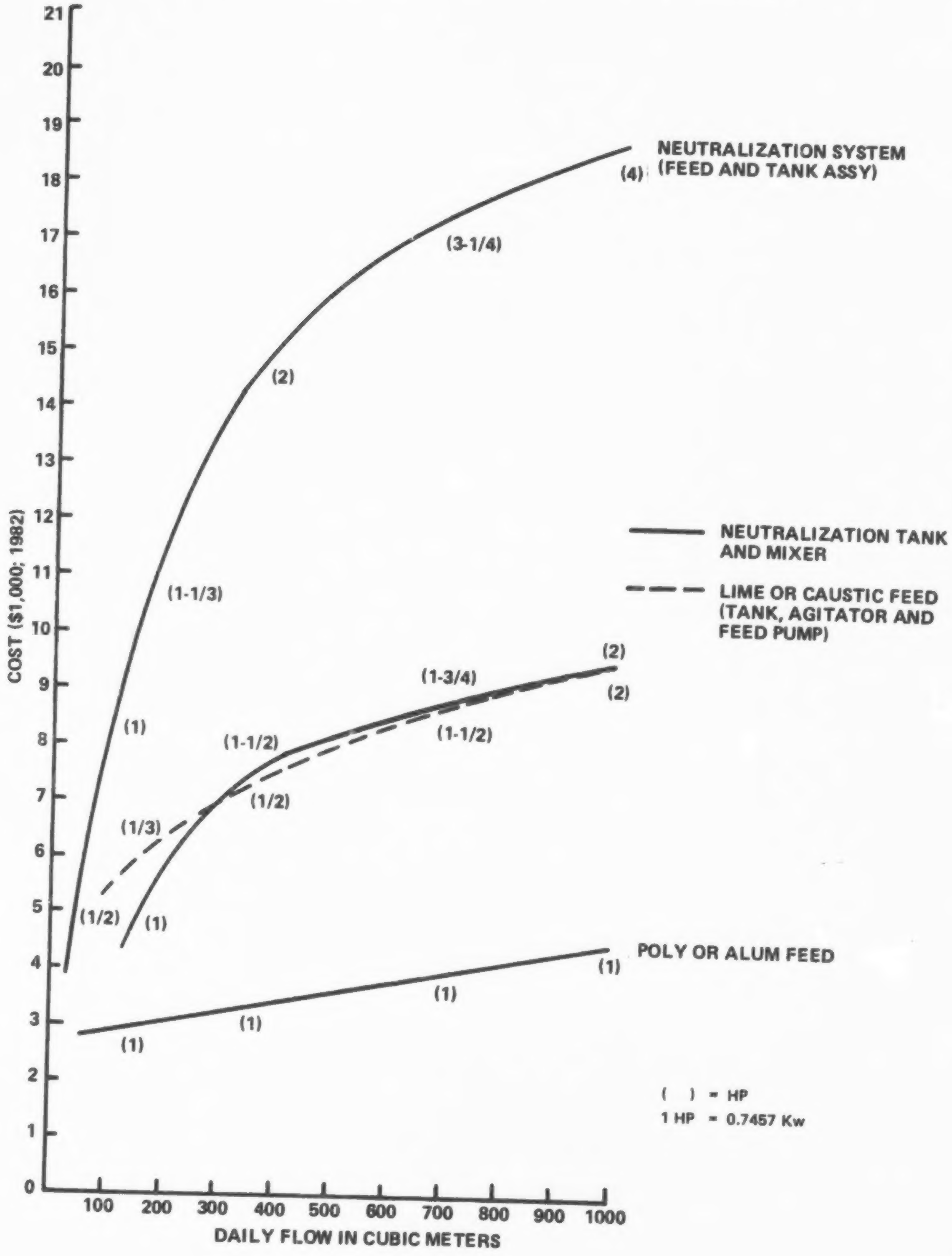
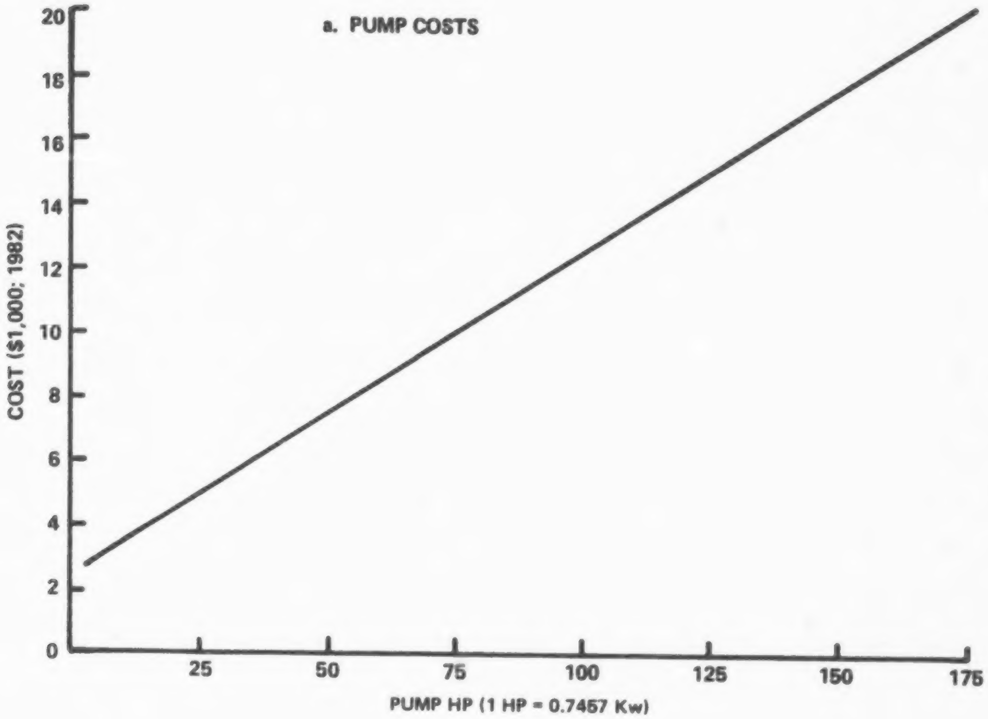


Figure 10-8. PUMP AND CHROME REDUCTION SYSTEM COSTS


a. PUMP COSTS

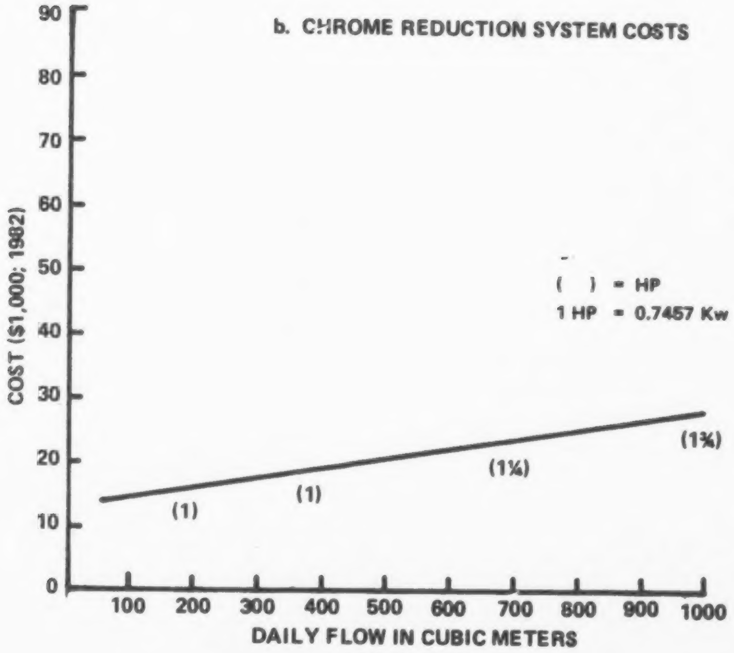

b. CHROME REDUCTION SYSTEM COSTS

Figure 10-9. FILTER PRESS COSTS

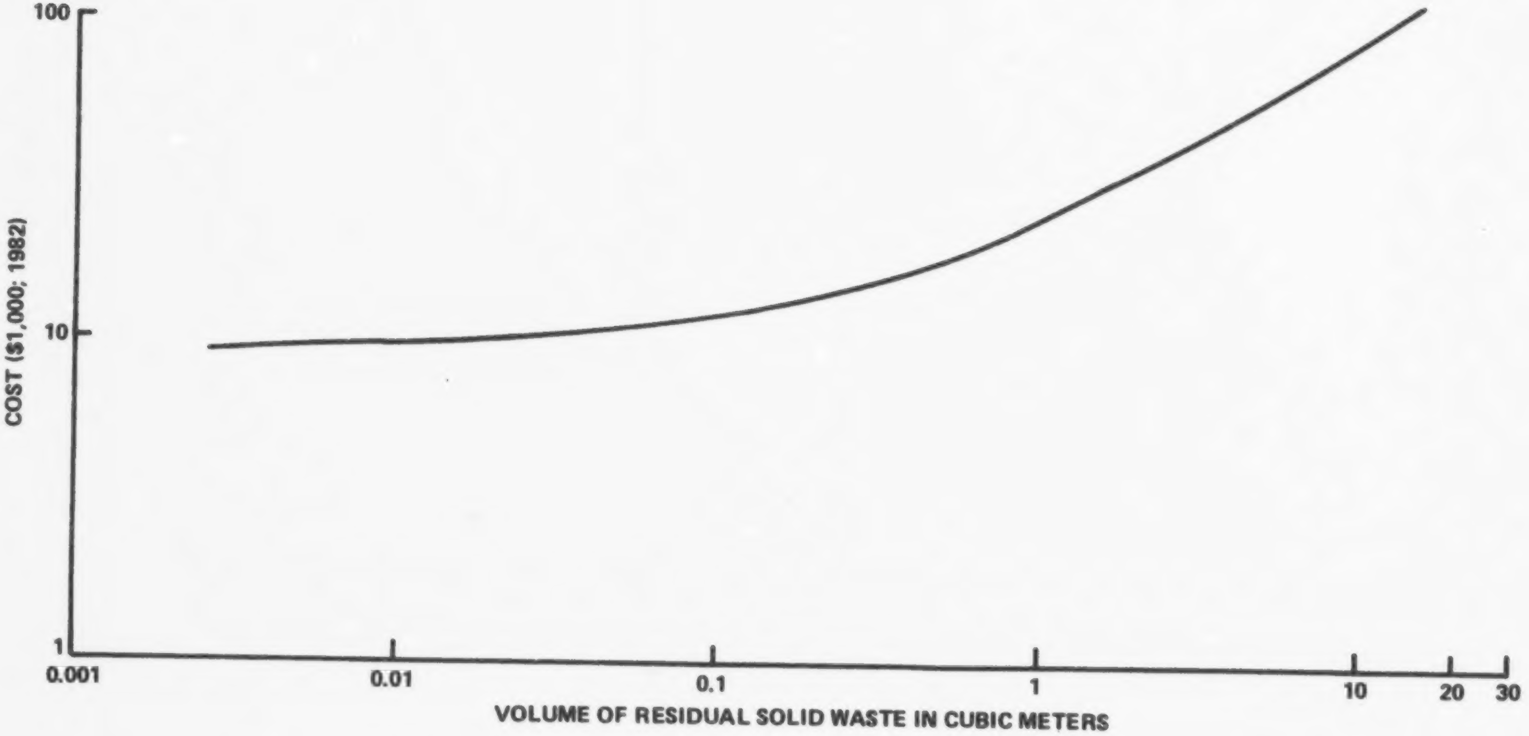


Figure 10-10 Alkaline Precipitation, Settling, pH Adjustment, Sludge Dewatering

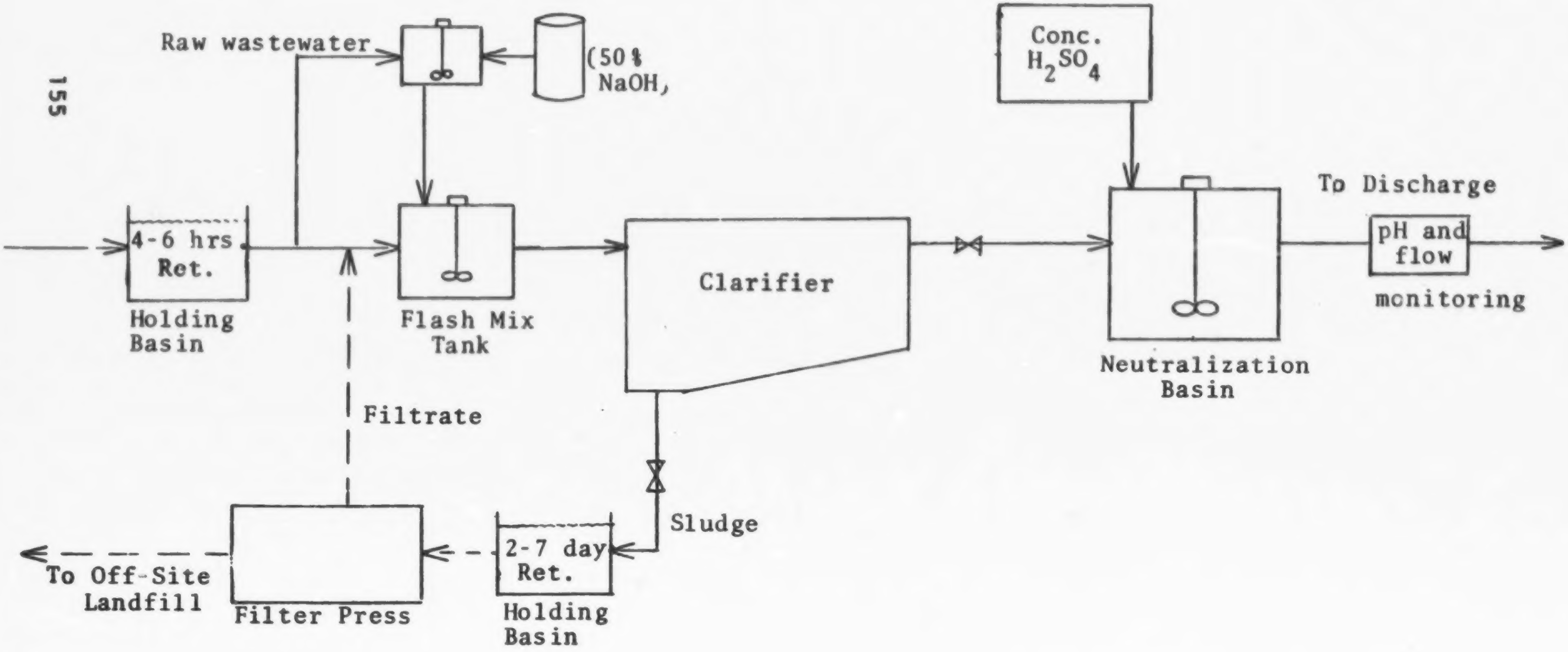

Raw wastewater
(50%
NaOH,
Conc.
H_2SO_4
To Discharge
4-6 hrs
Ret.
Holding
Basin
Flash Mix
Tank
Clarifier
pH and
flow
monitoring
Neutralization
Basin
Filtrate
Sludge
2-7 day
Ret.
To Off-Site
Landfill
Filter Press
Holding
Basin

Figure 10-11. Granular Media Filtration

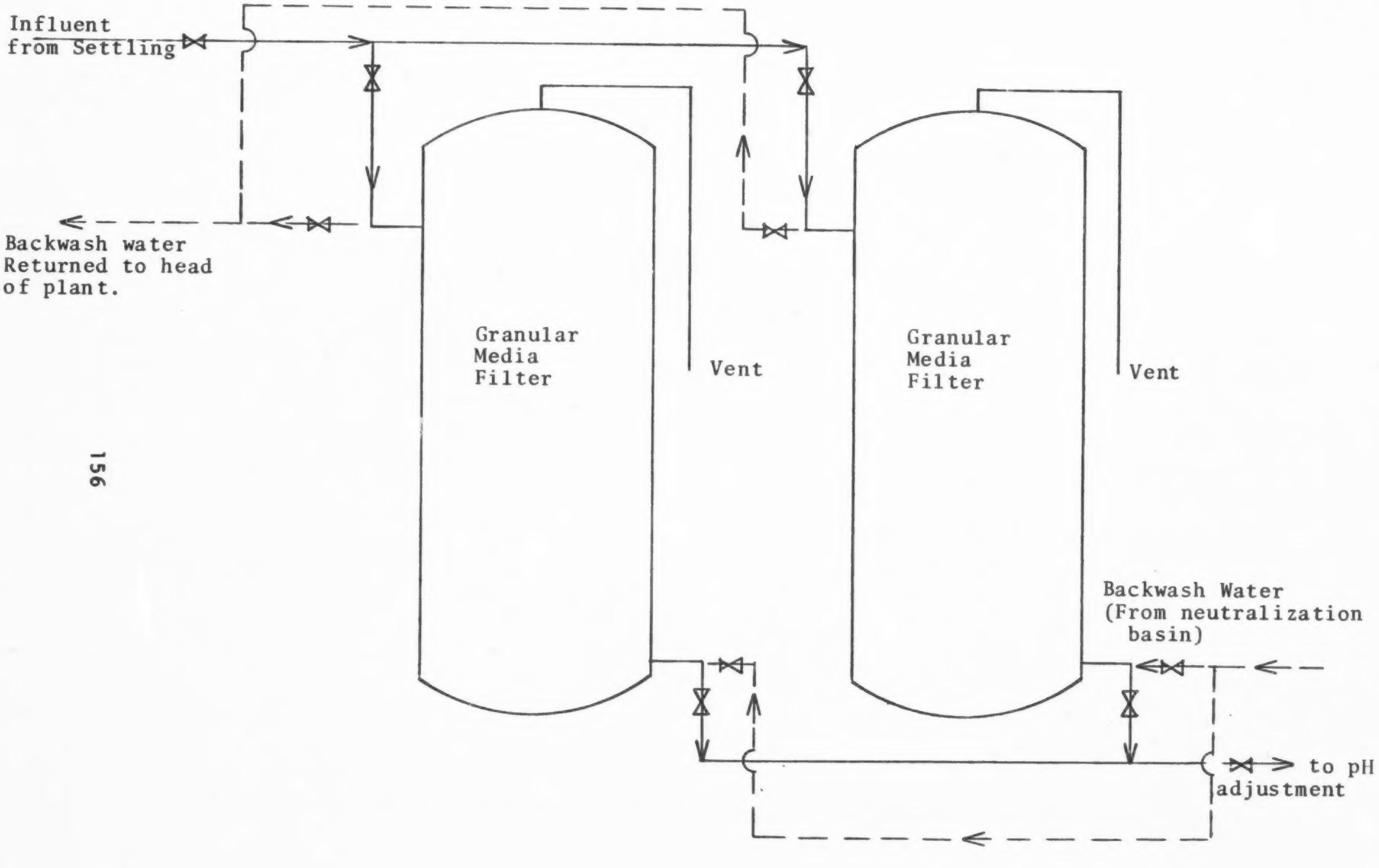

Influent
from Settling
Backwash water
Returned to head
of plant.
Granular
Media
Filter
Vent
Granular
Media
Filter
Vent
Backwash Water
(From neutralization
basin)
to pH
adjustment

Figure 10-12. Alkaline Precipitation, Settling, pH Adjustment (Batch Process)

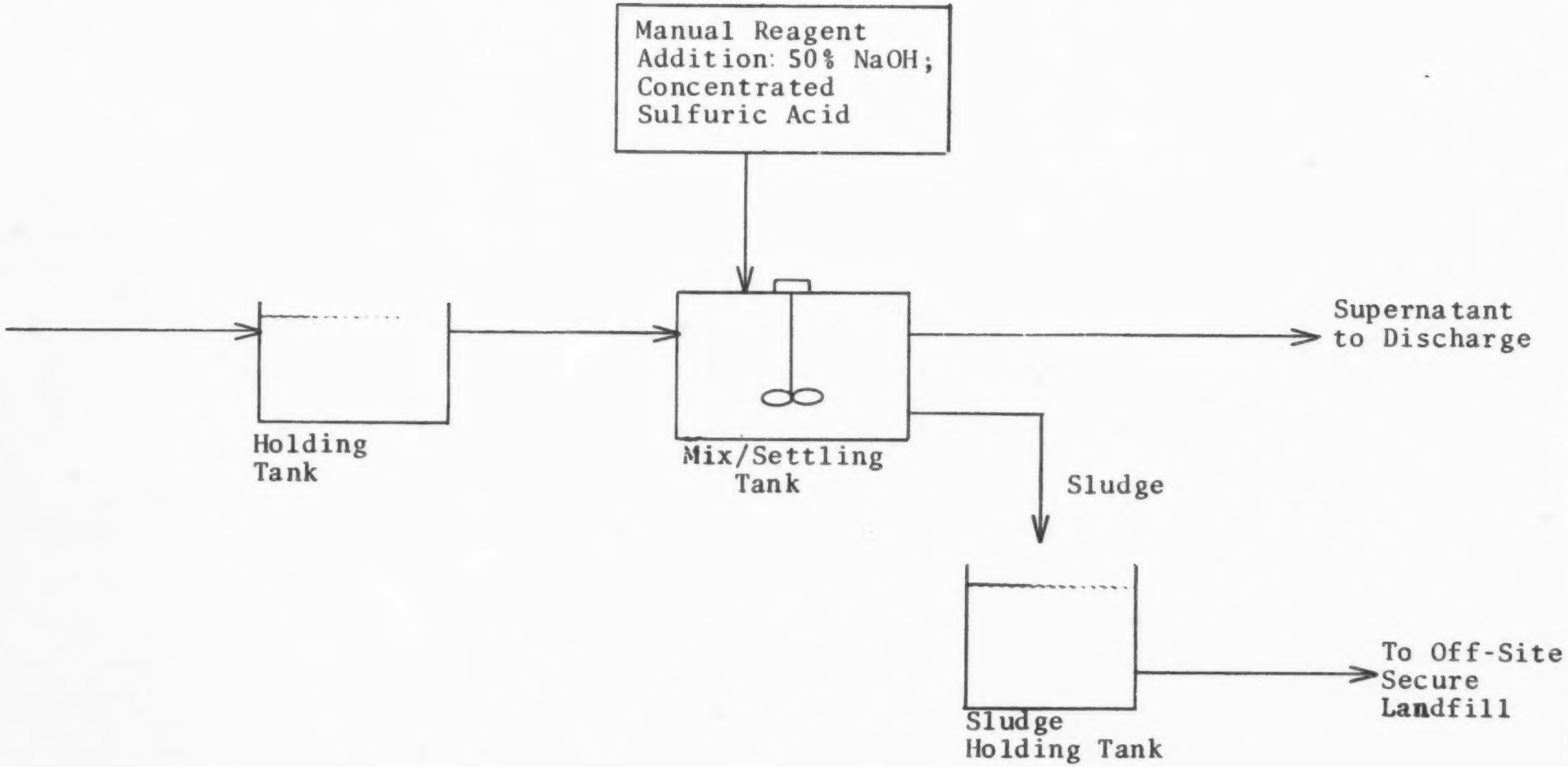

Manual Reagent Addition: 50% NaOH; Concentrated Sulfuric Acid
Holding Tank
Mix/Settling Tank
Supernatant to Discharge
Sludge
Sludge Holding Tank
To Off-Site Secure Landfill

Figure 10-13. Granular Media Filtration (Batch Process)

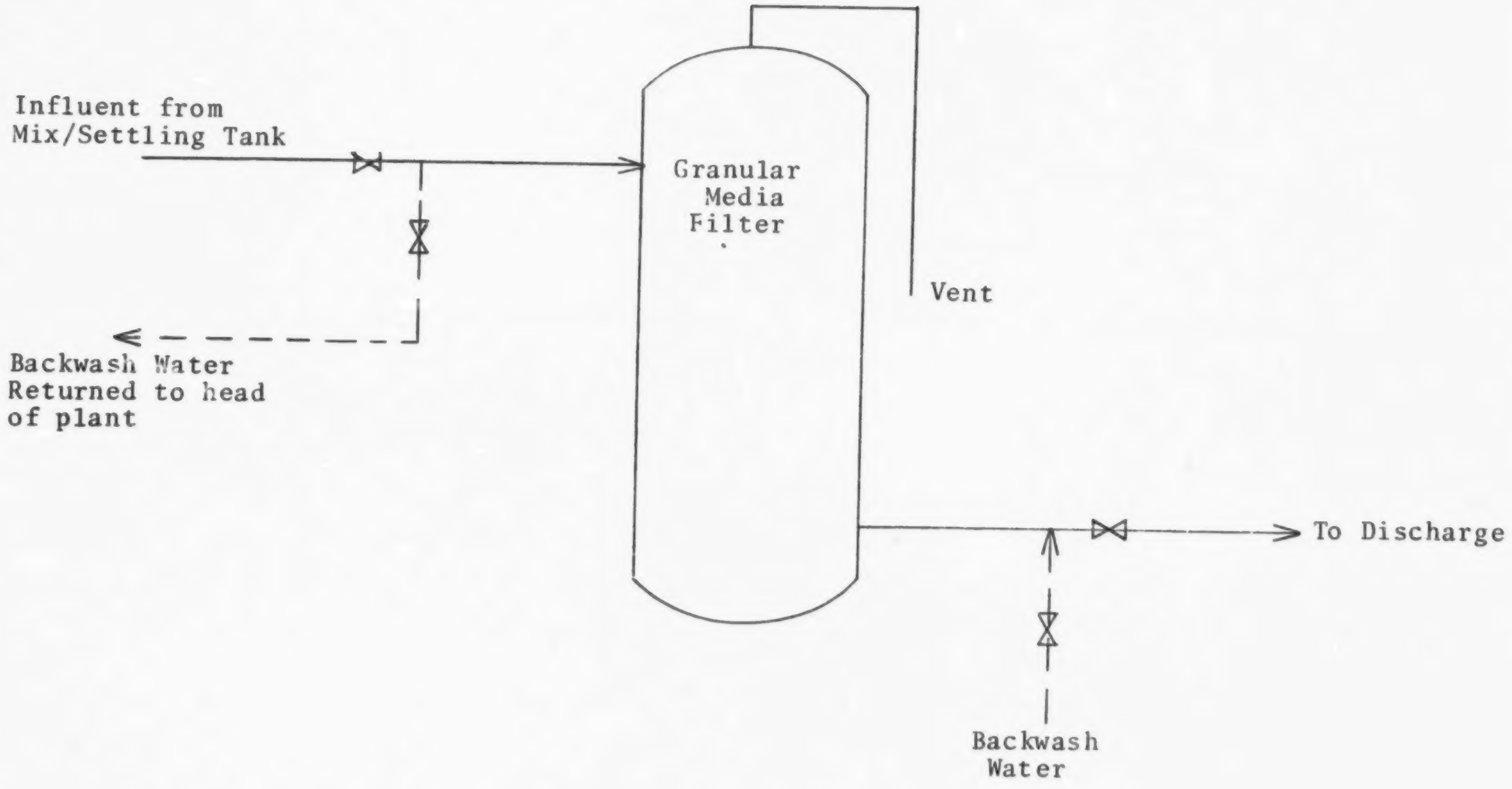
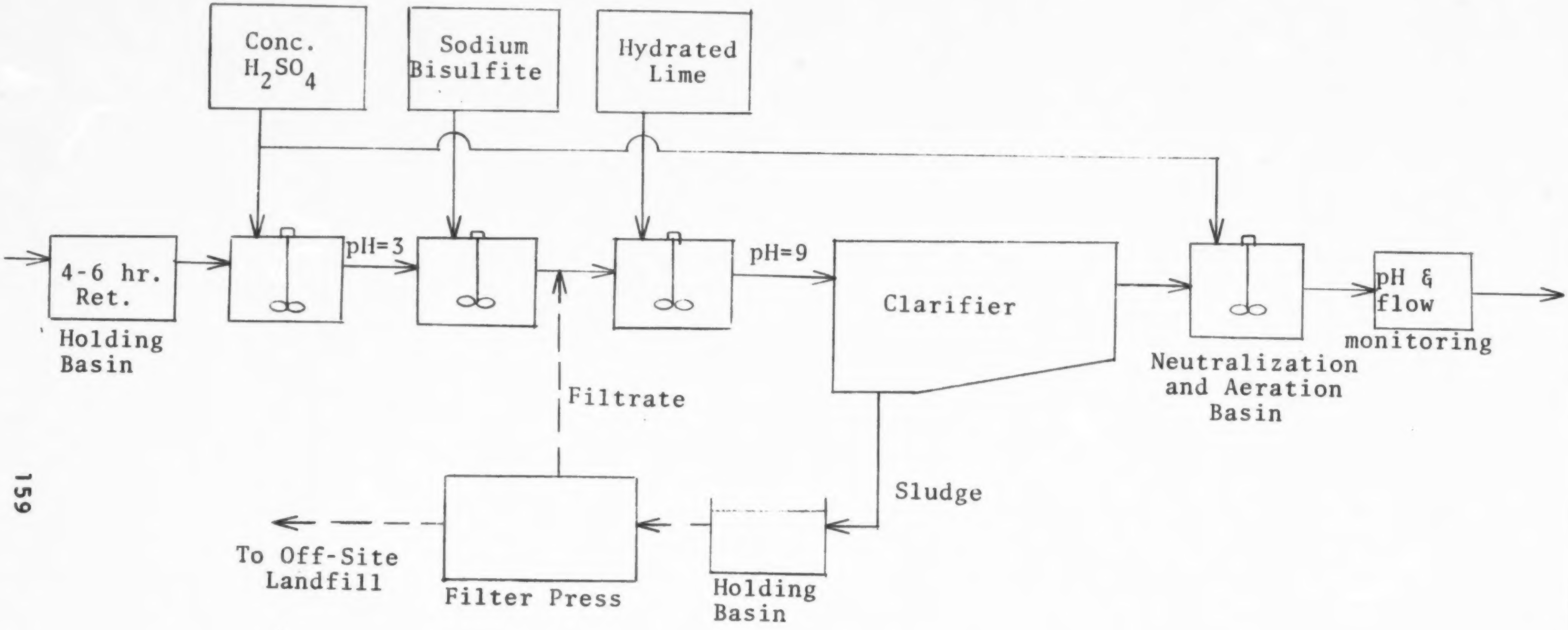

Influent from
Mix/Settling Tank
Granular
Media
Filter
Vent
Backwash Water
Returned to head
of plant
To Discharge
Backwash
Water

Figure 10-14. Chromium Reduction, Alkaline Precipitation, Settling, Final pH Adjustment and Sludge Dewatering


Conc.
H_2SO_4
Sodium Bisulfite
Hydrated Lime
4-6 hr. Ret.
Holding Basin
pH=3
pH=9
Clarifier
pH & flow
monitoring
Neutralization and Aeration Basin
Filtrate
Sludge
To Off-Site Landfill
Filter Press
Holding Basin

Operating Personnel. Personnel costs are based on an hourly rate of $25.00. This includes fringe benefits, overhead and supervision. Personnel are assigned to specific activities as required.

Maintenance and Repair. Cost of facility and equipment repair and maintenance is estimated as 10 percent of the total capital cost, excluding land.

Materials. The materials employed in the treatment processes and their costs are shown below. Unit costs of the materials were obtained from vendors and the Chemical Marketing Reporter. Representative transportation costs were added to arrive at the following material costs.

Soda, Caustic Liquid (50%)	$375/metric ton
Sulfuric Acid (100%)	$ 60/metric ton
Lime, Hydrated	$ 65/metric ton
Sodium Bisulfite	$720/metric ton
Soda Ash	$130/metric ton

Energy. Electricity costs are based on horsepower ratings, computed as follows:

$$Cy = 1.1\,(HP \times .7457 \times Hr \times Ckw)/(E \times P)$$

where:

Cy = Annual cost
1.1 = Allowance factor for miscellaneous energy use
Hr = Annual operating hours

HP = Total horsepower rating of motors (1 HP = 0.7457 kw)
Ckw = Cost per kilowatt hour of electricity ($0.06)
E = Efficiency factor (0.9)
P = Power factor (1.0)

This yields a cost of $328 per horsepower assuming operations are conducted 24 hours per day, 250 days per year. Adjustments are made for increased operating days and for batch process operations.

The cost of steam, where employed in the treatment process, is estimated to cost $22 per 1000 kg at 689.5 kPa ($10 per 1000 lb at 100 psi).

Residual Waste Disposal. Sludge disposal costs can vary widely depending on the characteristics and bulk of the waste. Off-site hauling and disposal costs are estimated as $60 per cubic meter

($46 per cubic yard) for deposit in a secure landfill (permitted for hazardous material) and $15 per cubic meter ($11.50 per cubic yard) for deposit in a sanitary landfill. The cost of containerized (drummed) waste disposal in a secure landfill is $160 per cubic meter ($123 per cubic yard). This is based on a cost of $20 for a 0.2 cubic meter (55 gallon) drum.

On-site waste disposal is based on land valued at $30,000 per hectare ($12,000 per acre). The work is assumed performed by an outside contractor at a cost of $360 per day or $855 per week for a 1.15 cubic meter (1½ cubic yard) front end loader and $725 per day or $2,525 per week for a 1.15 cubic meter (1½ cubic yard) bucket clamshell.

Monitoring, Analysis and Reporting. The manpower requirements covered by the annual labor and supervision costs include those activities associated with the operation and maintenance of monitoring instruments, recorders, automatic samplers and flow meters. Additional costs for analytical laboratory services have been estimated assuming that samples are analyzed once a week at the point of discharge and that an analytical cost of $20 per constituent is incurred. The determination of six constituents is assumed. The addition of a nominal reporting cost yields an annual cost of $8,000; this cost is applied except where noted otherwise.

Taxes and Insurance. An annual provision of 3 percent of the total capital cost has been included for taxes and insurance.

Amortization

Annual depreciation and capital costs are computed as follows:

$$C = (B(r)(1+r)^{n}) \div ((1+r)^{n}-1)$$

Where:

C = Annual Cost
B = Initial amount invested excluding cost of land
r = Annual interest rate (assumed 10%)
n = Useful life in years

The multiplier for B in the equation is often referred to as the capital recovery factor, and is 0.1627 for the assumed overall useful life of 10 years. No residual or salvage value is assumed.

Batch Processing of Wastewater

The quantity of wastewater generated in the production of the inorganic chemicals considered in this report varies widely from as little as 0.07 m^3 to 1,000 m^3 per day. Batch rather than continuous wastewater treatment is used for the small flows. Where batch processing is employed, it is so indicated.

There is a trade-off in batch processing between equipment size and the frequency with which treatment operations are performed.

ACCURACY OF ESTIMATES

Errors in the cost estimates can arise from a number of sources. The actual equipment costs are based largely on vendor quotations and thus represent current prices. The cost estimating relationship used to derive settling pond construction costs was validated by comparing actual costs incurred by a local contractor in the construction of several sized settling ponds, with costs for similarly sized impoundments, as estimated with the cost estimating relationship. The cost difference was less than 10 percent.

The installation material and labor constitute approximately 25 to 30 percent of the total system costs. Since these costs are extremely site-specific, errors as large as 50 to 100 percent can occur in selected instances. It should be noted that this magnitude of error would result in a total system error in the order of ±25 percent.

The largest source of error in this report arises from the simplifying assumption that the plants producing the chemicals are single product plants. In fact, most of the chemicals are manufactured in multi-product plants and may be produced only intermittently during the year. Specific plant operation data would be needed to determine which treatment modules or fractions of such module costs should be assigned to the treatment costs of specific chemicals.

In the absence of such information, it is not possible to quantify the error range for this source of error. It is believed that the costs developed in this study are generally somewhat greater than those that would be incurred by individual plants which comprise the industry because the costs do not include the economies of scale that result when wastewaters from several products are treated in a common treatment system. The Economic Impact Analysis does take those economies into account.

DESCRIPTION OF WASTEWATER TREATMENT TECHNOLOGIES

The technologies considered for the treatment of effluent wastewater streams of the model plants are described in this section. Schematics of the treatment technologies are provided. They form the bases for the model plant capital and annualized costs presented in the section that follows (Model Plant Treatment Costs).

Alkaline Precipitation, Settling, pH Adjustment, Sludge Dewatering

This treatment system is shown in Figure 10-10. A holding basin sized to retain 4-6 hours of flow is provided at the treatment system in-flow. The function of this basin is to provide a safeguard in the event of treatment system shut-down for scheduled or unscheduled maintenance.

The initial treatment step is the addition of caustic soda. This is followed by clarification/settling. If the wastewater characteristics are suitable, a tube settler may be substituted for a clarifier. It has the advantage of lower space requirements and is generally less expensive than a clarifier. Provisions for backwashing the tubes (if clogged) should be included. Treated supernatant would be used to backwash the tube settlers, and the backwash water should be returned to the head of the plant for treatment. The sludge is removed from the clarifier and directed to a filter press for dewatering. Pits are provided at the filter press for the temporary storage of sludge and the resultant dewatered residual material. The latter is assumed to be periodically transported to a secure landfill. The pH of the clarified wastewater stream is adjusted to an acceptable level by acid addition prior to discharge if necessary.

A monitoring system is installed at the discharge point.

Granular Media Filtration

Further removal of metal hydroxide precipitates and other solids from the wastewater can be achieved by sand filtration as shown in Figure 10-11. A granular media filter generally provides better removals of solids than is achieved with a filter press and therefore the costs used to estimate total system costs are based on granular media filters.

Alkaline Precipitation, Settling, pH Adjustment (Batch Process)

The treatment technology is essentially similar to that described in the previous section. It is shown in Figure 10-12. The batch process is employed in plants characterized by low wastewater flow. Again, a holding basin is provided at the head of the treatment system. The system consists of a mixing/settling tank to which the reagents, NaOH for alkaline precipitation and H_2SO_4 for final pH adjustment prior to discharge, are added manually.

In most cases, the quantity of sludge formed is very small; too small to justify the addition of a filter press. A holding tank is provided for the temporary storage of the wet sludge prior to its shipment to a secure landfill.

Granular Media Filtration (Batch Process)

This technology is an add-on to the above and is shown in Figure 10-13. It consists of a small sand filter through which the wastewater flows prior to discharge.

Hexavalent Chromium Reduction, Alkaline Precipitation, Settling, Final pH Adjustment, and Sludge Dewatering

This technology is shown in Figure 10-14. A retention pond or pit, depending on the size of wastewater stream, is installed at the head of the treatment system. The wastewater stream is initially treated with acid to reduce the pH to the level required for chromium reduction (CrVI to CrIII). This scheme would be utilized only in the sodium chlorate subcategory. Sodium bisulfite is added to accomplish the reduction of hexavalent chromium. Hydrated lime is then added to precipitate the chromium at a pH of 8 to 9. The wastewater is then directed to a clarifier. The sludge is removed and a filter press is employed for sludge dewatering. Pits are provided for the temporary retention of the sludge and the "dry" cake prior to the latter's shipment to a hazardous material landfill. The pH of the clarified wastewater stream is adjusted to an acceptable level by acid addition if necessary prior to discharge.

A monitoring system is installed at the discharge point.

Chlorine Destruction

This is achieved by the addition of sodium bisulfite. Given that the treatment technology described above (hexavalent chromium reduction, etc.) is in place, no additional equipment is required. Chlorine reduction is achieved by an increase in the amount of sodium bisulfite used (see Figure 10-14).

Dual-Media Filtration

In cases of high flow systems, dual-media filters can be used to increase the total filtration capacity. In general, dual-media filters exhibit greater capacity than single media filters, thus increasing the length of filter runs prior to backwashing. In extremely large systems this can mean less spare capacity and less maintenance time. However for the purposes of this analysis, there is not a significant difference in costs due to these factors.

MODEL PLANT TREATMENT COSTS

General

On the basis of hypothetical model plant specifications (production, flow, etc.), the capital and annual costs for various wastewater treatment options have been estimated for each of the six subcategories. The rationale for selection of model plants for each subcategory is presented in Sections 11 through 16.

Capital and annualized costs for model plant wastewater treatment systems for each subcategory are presented in tabular form in the specific subcategory sections (Sections 11-16). Specifically, the costs are for the treatment systems described in Figures 10-10 to 10-14 and are based on the costs, cost factors and assumptions documented previously in this section.

As noted in this section, facilities include items such as buildings, ponds and concrete pits. The buildings provided are sufficiently large so that space is available for additional equipment which may be required for additional treatment. In most instances, equipment requirements for additional treatment are relatively small compared to those proposed for the basic or initial wastewater treatment scheme.

Equipment costs shown in the cost tables include the cost of installation, materials, and labor as well as instrumentation. The remaining capital cost categories shown in these tables are self-explanatory.

The annualized costs shown in the cost tables are presented under three major headings: amortization, operations and maintenance, and solid waste disposal. The amortization cost is derived from the capital cost less the cost of land. Operations and maintenance costs include the following costs: personnel, facility and equipment repair and maintenance, reagents, energy, taxes and insurance.

Solid wastes generated in the treatment processes are considered hazardous and are assumed to be disposed of in secure landfills (permitted for hazardous wastes).

In the Cadmium Pigments and Salts subcategory, two model plants were chosen, one representing the cadmium pigments segment and the other representing the cadmium salts segment. In each case, two treatment options were considered (see Section 11).

In the Cobalt Salts subcategory, only one model plant was chosen because production is relatively low and a small amount of wastewater is generated from the production processes. Two treatment alternatives were considered (see Section 12).

Model plants used in the Copper Salts subcategory were based upon copper carbonate production and upon other copper salts production due to the large disparity in unit flow characteristics. Two model plants were chosen, one representing each segment, and the costs for two treatment alternatives for each model plant were estimated in Section 13.

The Nickel Salts subcategory was also represented by two model plants based upon large differences in unit flow values. One model plant represents production of nickel carbonate, while the other represents production of the other nickel salts. Model plant costs, consisting of two treatment alternatives for each model plant, are presented in Section 14.

The Sodium Chlorate subcategory is represented by one model plant. Model plant costs for two treatment alternatives are presented in Section 15.

Two model plants were chosen to represent the Zinc Chloride subcategory. Two treatment alternatives were costed for this subcategory (See Section 16).

Two subcategories were considered for BAT revisions, sodium chloride and sodium sulfite. Detailed costs for various alternatives are presented in Section 17 - "BAT Revisions."

SAMPLE MODEL PLANT COST CALCULATION

General

The subsection which follows outlines the methodology which is used to derive the estimated costs for various levels of technology which might be employed typically in the Phase II chemicals group. The example given is for a hypothetical plant, but a number of Phase II plants producing a variety of products would encounter a similar situation where wastewater from those products are commingled for treatment.

This subsection demonstrates individual system component cost estimating procedures. If a particular design should vary from the system description given, it would be possible to follow the procedures given for those system components which are the same making appropriate substitutions for any differences. For example, a company might use a fabricated steel tank for holding sludge in place of the concrete sludge pit specified. The remainder of the system would be costed according to the methodology shown while the cost of the concrete pit would be replaced by the cost of the steel tank. Similarly, if a lime feed system were chosen rather than a sodium hydroxide system, the capital costs and reagent costs could be substituted in the place of those given.

Sample Calculation

The model plant considered produces 4,800 kkg of metal salts annually and discharges 300 m^3 of wastewater daily. Two treatment levels are considered. Treatment is performed on a continuous basis. The plant is assumed to operate 24 hours per day, 350 days per year.

Level 1: Alkaline precipitation, clarification, sludge dewatering and pH adjustment.

Two concrete pits are constructed at the wastewater intake for the temporary retention of wastewater. A caustic solution (NaOH, 50 percent solution) is added to the wastewater at a rate of 1.33 kg per cubic meter before clarification. Sludge from the clarifier is dewatered in a filter press. Two concrete pits are provided for the temporary storage of sludge and dried filter cake. Approximately 0.22 cubic meters of filter cake are extracted daily and periodically shipped to a hazardous material landfill. Final pH adjustment of the wastewater is made utilizing sulfuric acid (H_2SO_4, 100 percent solution) before discharge. Instrumentation includes a pH meter and recorder, a flow meter and an automatic sampler. A building is provided for housing the system components.

Capital Costs:

	Cost	Source
Facilities		
Concrete wastewater holding pits (2-25 m^3)	$ 7,000	(Fig. 10-4a)
Concrete sludge pits (2-3 m^3)	1,600	(Fig. 10-4a)
Building (55 m^2)	18,000	(Fig. 10-4b)
Equipment		

NaOH feed system (300 m^3/day) (1 HP)	7,000	(Fig. 10-7)
Clarifier (300 m^3/day) (6 HP)	42,000	(Fig. 10-6)
Filter press (0.5 m^3)	18,000	(Fig. 10-9)
Neutralization system (300 m^3/day) (2 HP)	13,900	(Fig. 10-7)
Installation (materials and erection labor)	77,500	(p. 142)
Instrumentation	10,000	(p. 142)
Engineering (20%)	39,000	(p. 142)
Contractor overhead and profit (15%)	35,100	(p. 143)
Contingency (10%)	26,900	(p. 143)
Total Capital Costs	\$296,000	

Annual Costs:

Operating personnel (3.25 Hrs./Day at \$25/Hr.)	\$28,400	(p. 160)
Facility and equipment maintenance (10%)	29,600	(p. 160)
Materials		(p. 160)
NaOH (50% solution) (140 kkg/year)	52,500	
H_2SO_4 (100% solution)(5.25 kkg/year)	300	
Energy (9 HP)	4,100	(p. 160)
Monitoring and analysis	8,000	(p. 161)
Taxes and insurance (3%)	8,900	(p. 161)
Residual waste (77 m^3/Yr. at \$60/m^3)	4,600	(p. 160)
Amortization	48,200	(p. 161)
Total Annual Cost	\$184,600	

Level 2: Filtration

The wastewater flows through a sand filter before discharge.

Capital Costs:	Cost	Source
Facilities	None	
Equipment		
Sand filter (300 m^3/day)	\$15,800	(Fig. 10-6)
Installation (materials and erection labor)	15,100	(p. 142)
Engineering (20%)	6,200	(p. 142)

Contractor overhead and profit (15%)	5,600	(p. 143)
Contingency (10%)	4,300	(p. 143)
Total Capital Cost	$47,000	

Annual Costs:

Operating personnel (0.5 Hrs/Day at $25/Hr)	$ 4,400	(p. 160)
Facility and equipment maintenance (10%)	4,700	(p. 160)
Taxes and insurance (3%)	1,400	(p. 161)
Residual waste (2 m^3/yr at $60/$m^3$)	100	(p. 160)
Amortization	7,600	(p. 160)
Total Annual Cost	$18,200	

SECTION 10

REFERENCES

1. "Development Document for BAT Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry", prepared by Calspan ATC for USEPA Effluent Guidelines Division, September 1979.

2. "Building Construction Cost Data, 1982," by Robert Snow, Means Company, Inc.

3. "Modern Cost-Engineering Techniques," by Robert Popper, McGraw-Hill Book Company.

4. "Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category"
EPA 440/1-82/007, June 1982.

5. Vendor Quotations.

6. "Plant Design and Economics for Chemical Engineers", by M.S. Peters and K. D. Timmerhaus, McGraw - Hill Book Co., Third Edition.

SECTION 11

CADMIUM PIGMENTS AND SALTS INDUSTRY

INDUSTRIAL PROFILE

General Description

Cadmium pigments are a family of inorganic compounds primarily used as colorants in a number of industries and applications. These pigments have an important use in paints, where lead based paints cannot be used due to the presence of hydrogen sulfide in the environment. When hydrogen sulfide is present, it causes the formation of lead sulfide, which darkens the paint. Cadmium pigments are resistant to the effects of H_2S, high temperatures, and alkaline environments. For these reasons, they are also used in ceramics and glass, artists' colors, printing inks, paper, soaps and vulcanized rubber. Cadmium pigments vary somewhat in their chemical makeup depending on the colors. The various types include cadmium red, cadmium yellow, cadmium orange, cadmium lithopone red and cadmium lithopone yellow.

Cadmium salt compounds have wide and varied uses in industry. These include cadmium chloride which is used in photographic emulsions as a fog inhibitor, copying papers, dyeing, textile printing, as an ingredient in electroplating baths and as a catalyst. Cadmium nitrate is used principally by manufacturers of nickel-cadmium batteries and also as a catalyst and coloring agent in glass. Cadmium sulfate is used in electrolytic solutions for certain electrical elements and cells, and as a starting material for cadmium pigments.

Cadmium sulfide is the most important cadmium compound. It also occurs naturally combined with zinc ores. By itself, cadmium sulfide is used primarily as a yellow pigment. It is used in paints, ceramics, glass, soaps and paper and is also combined with other compounds to produce the cadmium pigments previously mentioned. Cadmium sulfide, when containing certain trace impurities, displays a very strong photoelectric effect and luminescent properties. These properties have wide applications across various industries. The industry data profile is given in Table 11-1.

There are 12 facilities producing cadmium compounds in this subcategory. Five of the producers manufacture cadmium pigments; however, pigment production is always associated with production of a precursor cadmium salt, predominately cadmium sulfate. The

TABLE 11-1. SUBCATEGORY PROFILE DATA FOR CADMIUM PIGMENTS AND SALTS

Number of Plants in Subcategory	12
Total Subcategory Production Rate	>4,000 kkg/yr
Minimum	NA
Maximum	>1,000 kkg/yr
Total Subcategory Wastewater Discharge	>1,200 m^3/day
Minimum	0
Maximum	450 m^3/day
Types of Wastewater Discharge	
Direct	6
Indirect	4
Zero	2

NA Not Available

remaining seven producers manufacture cadmium salts with no production of pigments.

Total annual production of cadmium pigments and salts is estimated to be in excess of 4,000 metric tons per year and total daily flow is estimated at greater than 1,200 cubic meters per day for all plants (flow attributed to cadmium pigments and salts production only). In 1977 cadmium sulfide pigment production alone accounted for approximately 1,950 metric tons according to the Bureau of the Census (1981 data unavailable).

General Process Description and Raw Materials

Cadmium Salts

Cadmium salts are produced by dissolving cadmium or its oxide in acid and evaporating to dryness. The starting material for all cadmium compounds is metallic cadmium. For special purposes, cadmium can be converted to cadmium oxide first. Cadmium salts are manufactured in batch modes usually for a certain number of days per year, depending on market demand.

The general manufacturing process for each of the above compounds is given below.

Cadmium chloride, cadmium nitrate, and cadmium sulfate are produced by dissolving cadmium metal or cadmium oxide in an aqueous solution of hydrochloric, nitric, or sulfuric acids respectively. The resulting solution can be used as is, but is usually evaporated to dryness to recover the solid product(1). The general reactions are:

$$Cd + 2HCl = CdCl_2 + H_2$$

$$Cd + 2HNO_3 = Cd(NO_3)_2 + H_2$$

$$Cd + H_2SO_4 = CdSO_4 + H_2$$

In the production of cadmium pigments, the resulting solution of cadmium sulfate may be used as is.

Cadmium Pigments

The basic component of cadmium pigments is the yellow-colored compound, cadmium sulfide, which is produced by the reaction of the purified cadmium sulfate solution with sodium sulfide in the strike (reaction) tanks. However, cadmium pigments are batch-produced to meet product specifications. Depending upon the shade of pigment desired, a variety of other materials may be

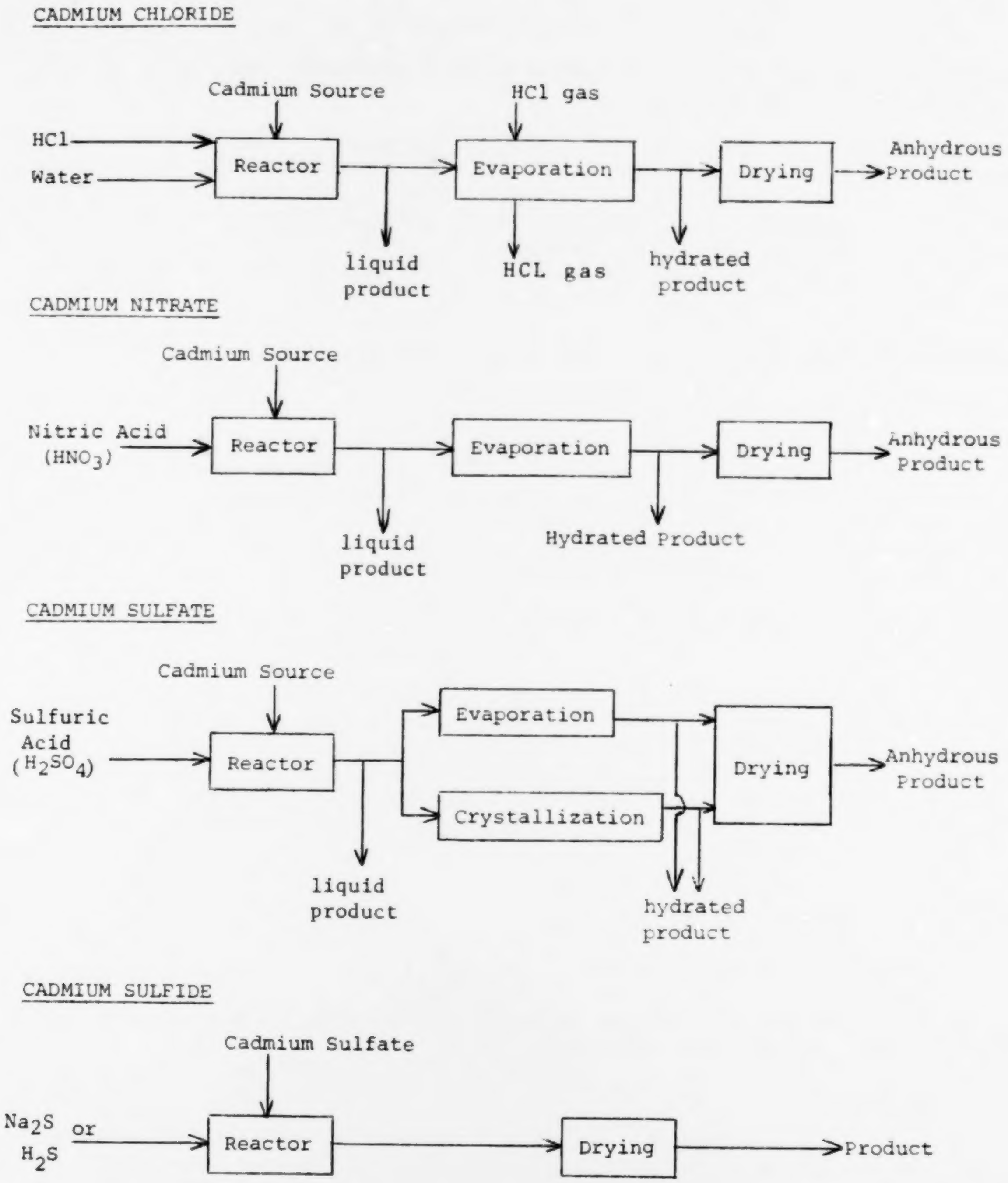
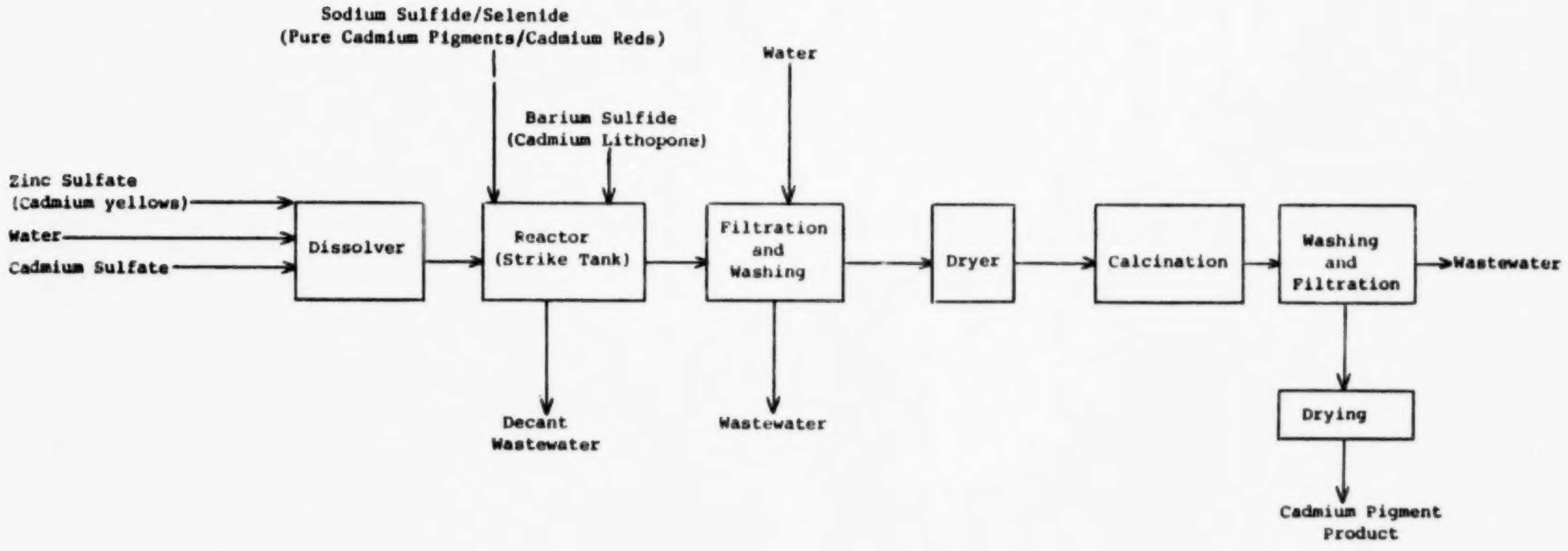

CADMIUM CHLORIDE
Cadmium Source
HCl gas
HCl
Water
Reactor
Evaporation
Drying
Anhydrous Product
liquid product
HCL gas
hydrated product
CADMIUM NITRATE
Cadmium Source
Nitric Acid (HNO3)
Reactor
Evaporation
Drying
Anhydrous Product
liquid product
Hydrated Product
CADMIUM SULFATE
Cadmium Source
Sulfuric Acid (H2SO4)
Reactor
Evaporation
Crystallization
Drying
Anhydrous Product
liquid product
hydrated product
CADMIUM SULFIDE
Cadmium Sulfate
Na2S or H2S
Reactor
Drying
Product

FIGURE 11-1. GENERALIZED PROCESS FLOW DIAGRAM FOR CADMIUM SALTS.



Sodium Sulfide/Selenide
(Pure Cadmium Pigments/Cadmium Reds)
Water
Barium Sulfide
(Cadmium Lithopone)
Zinc Sulfate
(Cadmium yellows)
Water
Cadmium Sulfate
Dissolver
Reactor
(Strike Tank)
Filtration
and
Washing
Dryer
Calcination
Washing
and
Filtration
Wastewater
Decant
Wastewater
Wastewater
Drying
Cadmium Pigment
Product

FIGURE 11-2. GENERALIZED PROCESS FLOW DIAGRAM FOR CADMIUM PIGMENTS.

added or co-precipitated with cadmium sulfide in the strike tank. Zinc is a common component of cadmium yellows. Cadmium sulfide and cadmium selenide are coprecipitated in the reaction tank to form cadmium red. Red and yellow lithopone pigments are manufactured by co-precipitating the pigments with barium sulfide. Another class of pigments may be obtained by co-precipitating mercury sulfide with cadmium sulfide. The normal running time per batch for cadmium pigment manufacturing is 10 days from strike to dry product. The number of operating days per year also depends on market demands. More detailed process descriptions and general reactions for the various pigment types are provided below.

Cadmium sulfide (cadmium yellow) is produced by the reaction of a sulfide source, usually sodium sulfide, with a solution of cadmium salt forming a precipitate of cadmium sulfide. Generally, cadmium sulfate is used as the cadmium salt source. The general reaction is:

$$CdSO_4 + Na_2S = CdS + Na_2SO_4$$

The production of cadmium pigments is more complex than is implied by the above equation. First, a soluble cadmium salt is produced by digesting cadmium metal in sulfuric acid. Nitric acid is often added to increase the reaction rate. The general reaction is:

$$8Cd + 9H_2SO_4 + 2HNO_3 = 8CdSO_4 + (NH_4)_2SO_4 + 6H_2O$$

The cadmium sulfate liquor is then purified in successive steps by addition of reagents and by filtration to remove iron, nickel, and copper impurities.

Cadmium Yellow (Pure)

This pigment is produced by reacting cadmium sulfate, sodium sulfide and zinc sulfate in the strike tanks. This pigment is a co-precipitated mix of cadmium sulfide and zinc sulfide, which gives it the distinct yellow color. The basic lemon yellow shade is essentially all cadmium sulfide as described above and the various different shades of yellow depend on the cadmium sulfide/zinc sulfide mix.

The basic general reaction is:

$$CdSO_4 + 2Na_2S + ZnSO_4 = CdS \bullet ZnS + 2Na_2SO_4$$

Cadmium Red (Pure)

The basic pure red pigment is produced by reacting a prepared solution of cadmium sulfate with a prepared solution of selenium metal in aqueous sodium sulfide together in the strike tanks to form a cadmium sulfoselenide complex. The amount of cadmium sulfide in the pigment determines the shade of red desired. The basic reaction is:

$CdSO_4 + Na_2SxSe(1-x) = CdSxSe(1-x) + Na_2SO_4$

(when x is always less than or equal to 1)

The variable subscript indicates the complex nature of this compound.

Cadmium Orange

This pigment is produced by blending cadmium reds and cadmium yellows until the desired shade is produced.

Cadmium Lithopone Pigments

Both the red and yellow cadmium pigments can be produced as lithopone pigments instead of pure. The reactions and processes are essentially the same. The difference is in the addition of barium sulfide to the strike tanks where it is reacted, and co-precipitated with the other chemicals previously mentioned.

The basic general reactions are, for red lithopone pigments:

$CdSO_4 + BaSx + Se(1-x) = CdSxSe(1-x) \bullet BaSO_4$ (when $x \leq 1$)

while the reaction for yellow lithopone pigments is:

$CdSO_4 + 2BaS + Zn\ SO_4 = CdS \bullet BaSO_4 \bullet ZnS + BaSO_4$

Regardless of which pigment is produced, the resulting precipitated pigments are decanted or filtered, washed, and dewatered in a filter. The pigments are subsequently dried and calcined for uniform color. Calcining emissions are generally scrubbed to capture pigment dust and sulfur dioxide. Final polishing steps vary from plant to plant, but the calcined pigments are usually quenched in water for washing and filtration. The pigment is again dried before blending and/or packaging. Generally the pigments are ground or crushed after drying. A general process diagram for the cadmium salts is given in Figure 11-1 while Figure 11-2 gives the general process diagram for cadmium pigments.

WATER USE AND WASTEWATER SOURCE CHARACTERISTICS

Water Use

In the cadmium salts industry, water is used primarily as the reaction medium. A small amount may be used in air pollution control (scrubbers) and in washdown of equipment and process areas.

In the cadmium pigments industry, water is used as the reaction medium (in the strike tanks) and to wash the pigments in several stages of production. Water is also used for maintenance and cleaning of filters and process areas. Water use varies from plant to plant for other process uses such as air pollution control equipment. These flows are minor compared to the direct contact process uses.

Normally, the production of pure pigments requires a longer washing period to wash out soluble impurities. This results in a larger water usage for this part of the process.

Table 11-2 is a summary of water usage at different cadmium salts plants while Table 11-3 summarizes water usage at different cadmium pigment plants.

Wastewater Sources

Wastewater flows from cadmium salt production vary from plant to plant and also vary for different products. In general, wastewater can emanate from decanted, filtered or purified reaction media, washdown of equipment and area, air pollution control devices and various other indirect process sources. These flows are minor compared to wastewater generated from pigment production. Table 11-4 summarizes wastewater flows from several cadmium salts plants.

At cadmium pigment plants, the different pigment products are manufactured concurrently on separate process lines and the wastewaters may be treated separately or combined for treatment and then discharged. Wastewater can originate from decanting or filtering the pigment slurry after it is precipitated in the strike vessels, and from secondary filtration during purification and finishing operations. The major sources of wastewater flow are from washing, quenching and rinsing the pigments. The quantity of wash and rinse water may be greater for some pigments than for others. A third source of wastewater includes the washing of the filters (primary and finishing) to remove pigments and impurities, especially when there is a color shade change in the production. Other sources of wastewater flow, which can vary

TABLE 11-2. WATER USAGE AT CADMIUM SALTS FACILITIES(1)

	Flow (m^3/kkg)		
	Plant Designation		
Water Use	F125(2)	F117(3)	F117(4)
Noncontact Cooling	0	0	0
Direct Process Contact	0.183	1.69	1.08
Indirect Process Contact	0	0	0
Maintenance	0	0	0
Air Pollution Scrubbers	0.0365	0	0
Noncontact Ancillary	0	0	0
TOTALS	0.219	1.69	1.08

(1) Values indicated only for those plants that reported separate and complete information.
(2) Cadmium Nitrate.
(3) Cadmium Sulfate (batch basis).
(4) Cadmium Chloride (batch basis).

Source: Section 308 Questionnaires and Plant Visit Reports

TABLE 11-3. WATER USAGE AT CADMIUM PIGMENTS FACILITIES(1)

	Flow (m^3/kkg)			
	Plant Designation(2)			
Water Use	F102	F101	F134	F110
Noncontact Cooling	0	34.4	0.116	0
Direct Process Contact	71.2	132.4	27.9	34.65
Indirect Process Contact	42.2	0	0	0
Maintenance	1.6	3.19	0.116	1.07
Air Pollution Scrubbers	1.07	<0.067	0.35	0
Noncontact Ancillary	0	0.16	0.87	0
TOTALS	116.1	170.2	29.35	35.7

(1) Values indicated only for those plants that reported separate and complete information.

(2) Values indicated were for all cadmium pigment production and include production of cadmium sulfate as starting material.

Source: Section 308 Questionnaires and Plant Visit Reports

TABLE 11-4. WASTEWATER FLOW AT CADMIUM SALTS FACILITIES(1)

	Flow (m^3/kkg)		
	Plant Designation		
Wastewater Source	F125(2)	F117(3)	F117(4)
Direct Process Contact	0	0	0
Indirect Process Contact	0	0	0
Maintenance	0	0.085	0.054
Air Pollution Scrubbers	0.036	0	0
TOTAL PROCESS WASTEWATER DISCHARGED	0.036	0.085	0.054
Noncontact Cooling	0	0	0
Noncontact Ancillary	0	0	0

(1) Values indicated only for those plants that reported separate and complete information.
(2) Cadmium Nitrate.
(3) Cadmium Sulfate.
(4) Cadmium Chloride.

Source: Section 308 Questionnaires and Plant Visit Reports

TABLE 11-5. WASTEWATER FLOW AT CADMIUM PIGMENTS FACILITIES(1)

Wastewater Source	Flow (m^3/kkg) Plant Designation(2) F102	F101	F134	F110
Direct Process Contact	71.2	132.4	25.5	34.65(3)
Indirect Process Contact	42.2	0	0	0
Maintenance	1.60	3.19	0.12	0
Air Pollution Scrubbers	1.07	0	NA	0
TOTAL PROCESS WASTEWATER DISCHARGED	116.1	135.6	25.62	0
Noncontact Cooling	0	34.4	0	0
Noncontact Ancillary	1.6	0.16	0.87	0

NA Flow volume not available.

(1) Values indicated only for those plants that reported complete information.

(2) Values indicated are for all cadmium pigments production and include production of cadmium sulfate as starting material.

(3) Discharge to on-site pond.

Source: Section 308 Questionnaires and Plant Visit Reports

from plant to plant, are maintenance and area washdowns and air pollution control devices. The sources of wastewater flow applicable to typical cadmium pigment plants are shown in the generalized flow diagram, Figure 11-3. The wastewater sources are similar for all pigment products. Table 11-5 presents the wastewater flow data summary for several cadmium pigment plants.

DESCRIPTION OF PLANTS VISITED AND SAMPLED

Eight facilities at which cadmium pigments and salts are manufactured were visited during the course of the program (many plants produce other Phase II products). Wastewater sampling was conducted at two of these plants.

Sampled Plants

Plant F102 produces several cadmium pigments by the process shown in Figure 11-3, and described above. The plant produces cadmium reds, cadmium yellows and cadmium orange pigments.

Wastewater emanates from a number of sources in the entire process. These consist of the reaction decants and direct rinse waters to wash out salts, filter washes, wet scrubbers and maintenance washdowns. Once-through noncontact cooling water is also used for washing the filters. Excess cooling water not needed to wash the filters is discharged with the other process wastewaters.

At the time of the sampling visit in 1980 all wastewater was collected in a sump, then was pumped to pigment plant treatment system (for cadmium recovery) and then discharged to the POTW. Cadmium treatment consisted of a 10,000-gallon equalization tank where caustic soda was added to raise the pH. A polyelectrolyte was added in a flash mix chamber and then the wastewater flowed to a tube settler. The overflow from the tube settler was discharged to an in-plant receiver, while the underflow was sent through a filter press for dewatering. The filter cake was collected and removed for cadmium recovery. At the time of sampling, the filtrate was combined with the tube settler overflow and discharged to a POTW without further treatment.

In 1982 the wastewater treatment system was changed. The discharge from the cadmium process treatment plant was commingled with other wastewater generated at the facility. The overflow from the tube settler was discharged to the main wastewater treatment facility, and the filtrate from the filter press sent to the beginning of the main wastewater treatment facility. The main wastewater treatment facility treats wastewater from the cadmium pigments plant (about 10 percent of the total flow) along

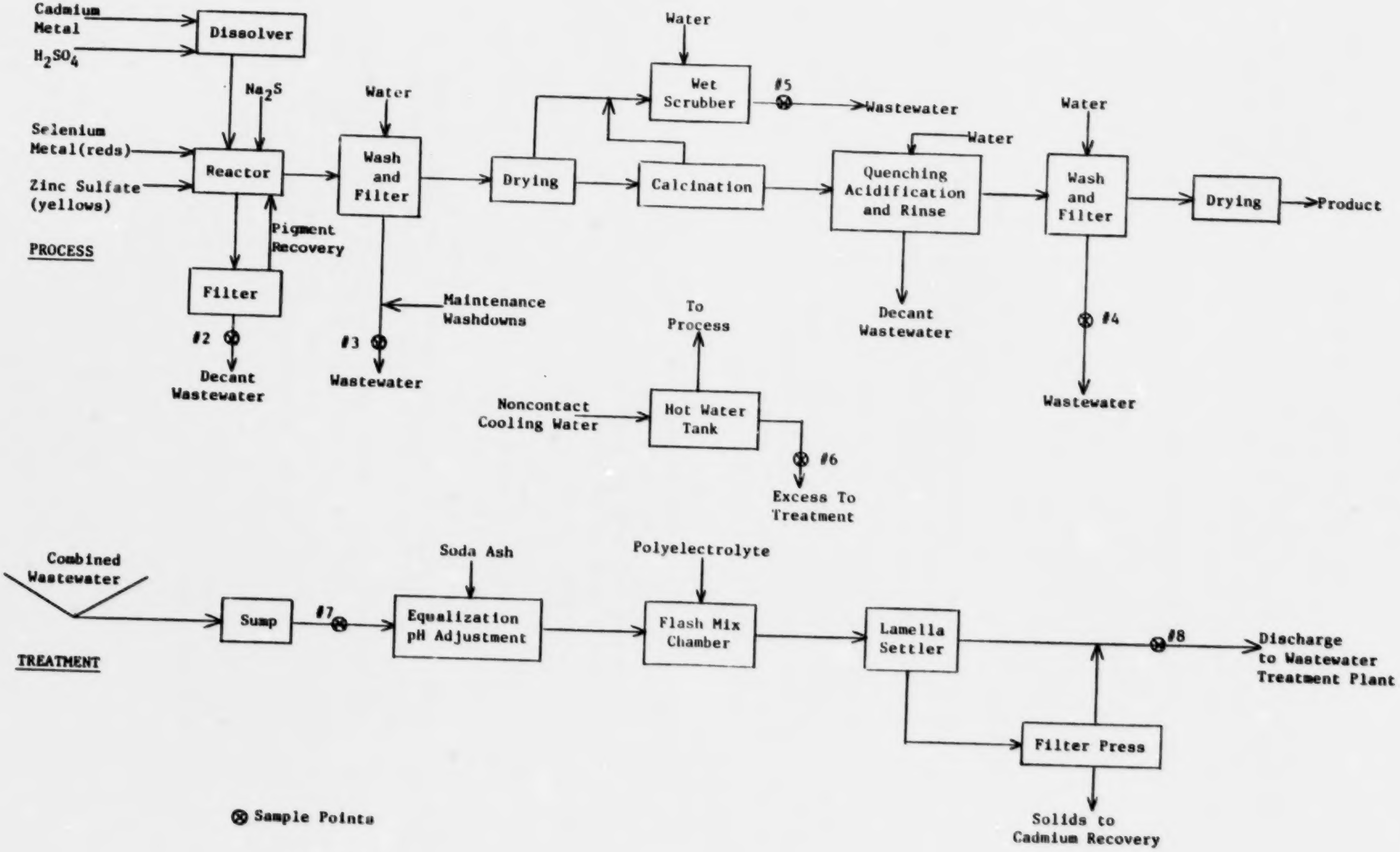
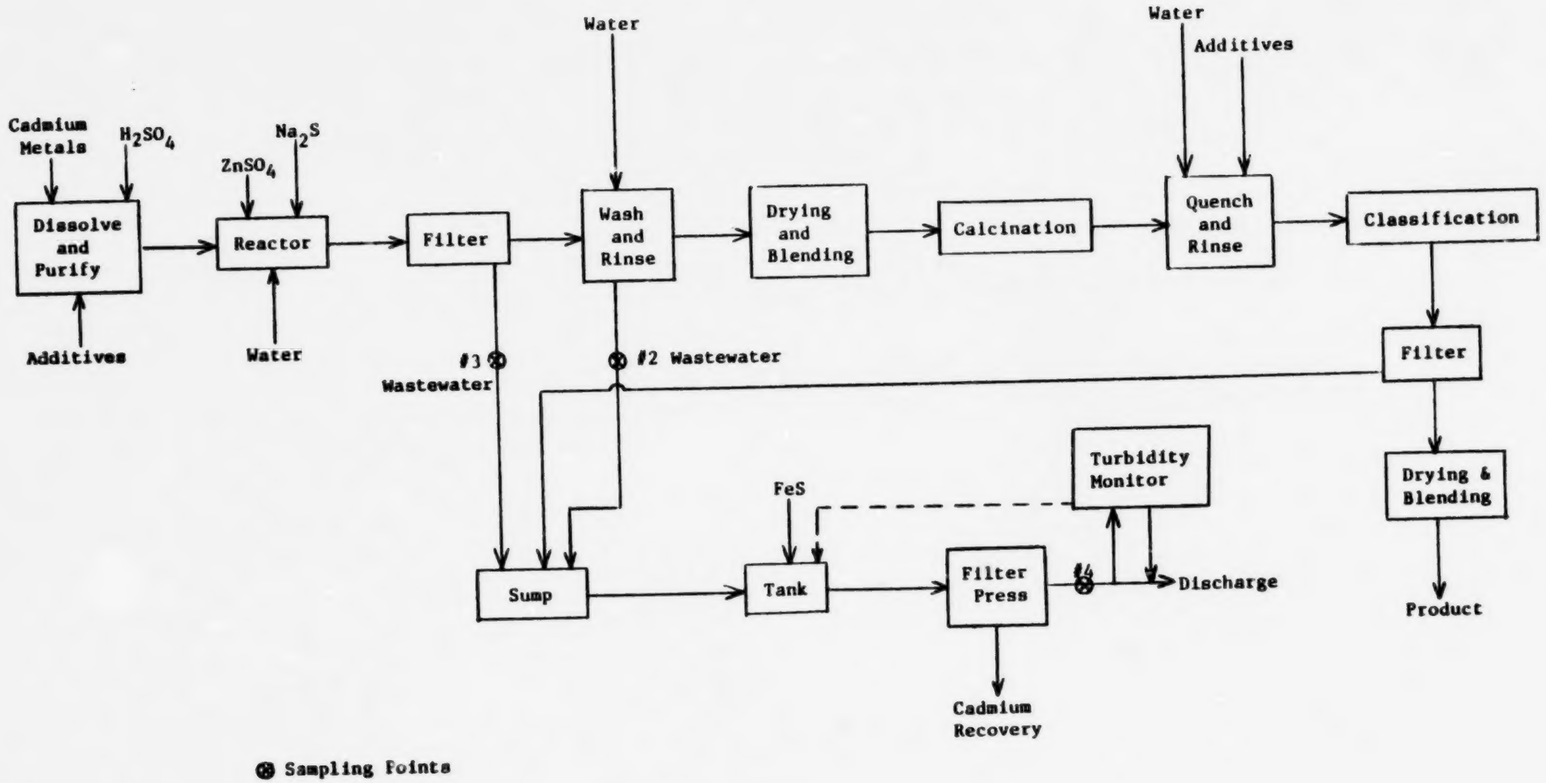

Cadmium Metal
H_2SO_4
Dissolver
Na_2S
Selenium Metal(reds)
Zinc Sulfate (yellows)
Reactor
Pigment Recovery
Filter
#2
Decant Wastewater
PROCESS
Water
Wash and Filter
Maintenance Washdowns
#3
Wastewater
Drying
Water
Wet Scrubber
#5
Wastewater
Calcination
Water
Quenching Acidification and Rinse
Decant Wastewater
Water
Wash and Filter
#4
Wastewater
Drying
Product
To Process
Noncontact Cooling Water
Hot Water Tank
#6
Excess To Treatment
Combined Wastewater
TREATMENT
Sump
#7
Soda Ash
Equalization pH Adjustment
Polyelectrolyte
Flash Mix Chamber
Lamella Settler
Filter Press
Solids to Cadmium Recovery
#8
Discharge to Wastewater Treatment Plant
⊗ Sample Points

FIGURE 11-3. PROCESS , WASTEWATER TREATMENT, AND SAMPLING LOCATIONS FOR PLANT F102

PURE YELLOW



Cadmium Metals
H_2SO_4
Dissolve and Purify
Additives
$ZnSO_4$
Na_2S
Reactor
Water
Filter
#3 Wastewater
Water
Wash and Rinse
#2 Wastewater
Drying and Blending
Calcination
Water
Additives
Quench and Rinse
Classification
Filter
Drying & Blending
Product
Sump
FeS
Tank
Filter Press
Cadmium Recovery
#4
Turbidity Monitor
Discharge
Sampling Points

FIGURE 11-4. PROCESS, WASTEWATER TREATMENT, AND SAMPLING LOCATIONS FOR PLANT F134.

LITHOPONE RED

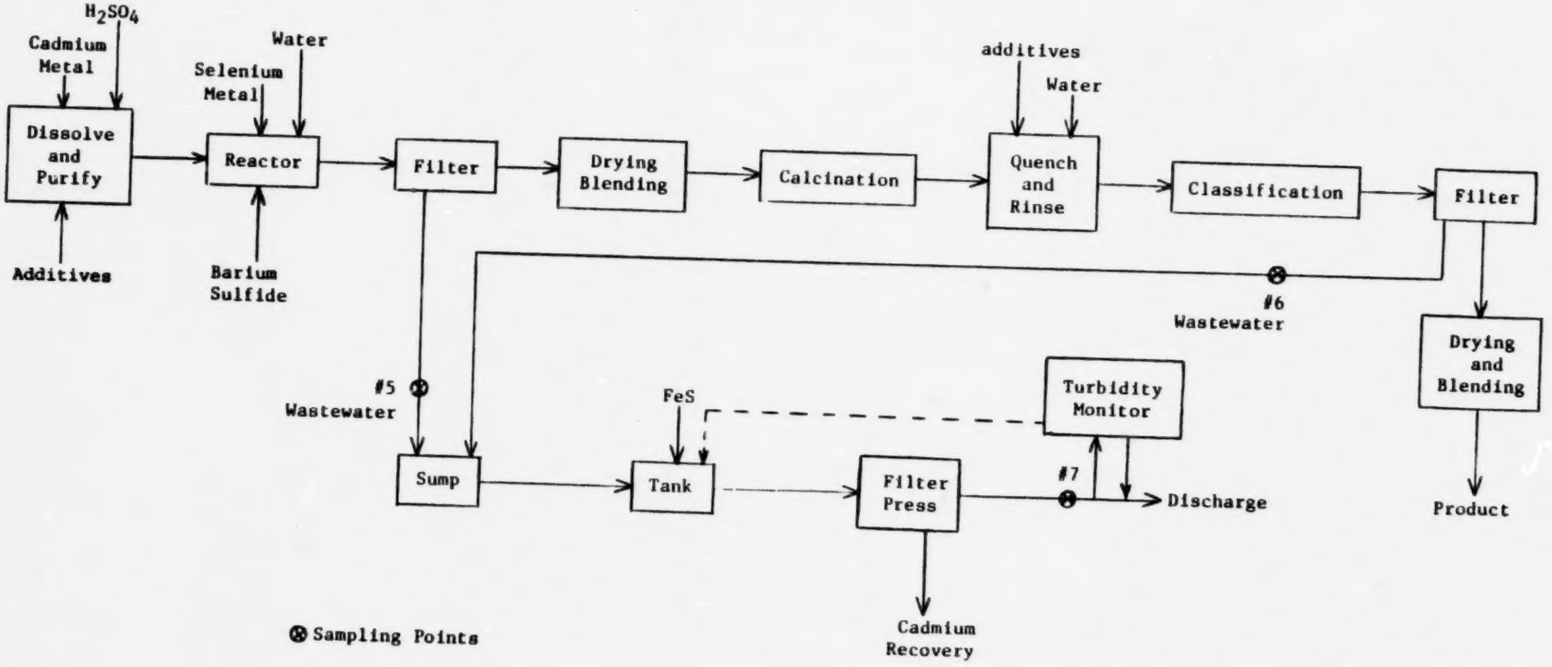

Cadmium Metal
H_2SO_4
Dissolve and Purify
Additives
Selenium Metal
Water
Reactor
Barium Sulfide
Filter
Drying Blending
Calcination
additives
Water
Quench and Rinse
Classification
Filter
Drying and Blending
Product
#6 Wastewater
#5 Wastewater
Sump
FeS
Tank
Filter Press
Cadmium Recovery
Turbidity Monitor
#7
Discharge
⊗ Sampling Points

FIGURE 11-5. PROCESS, WASTEWATER TREATMENT, AND SAMPLING LOCATIONS FOR PLANT F134

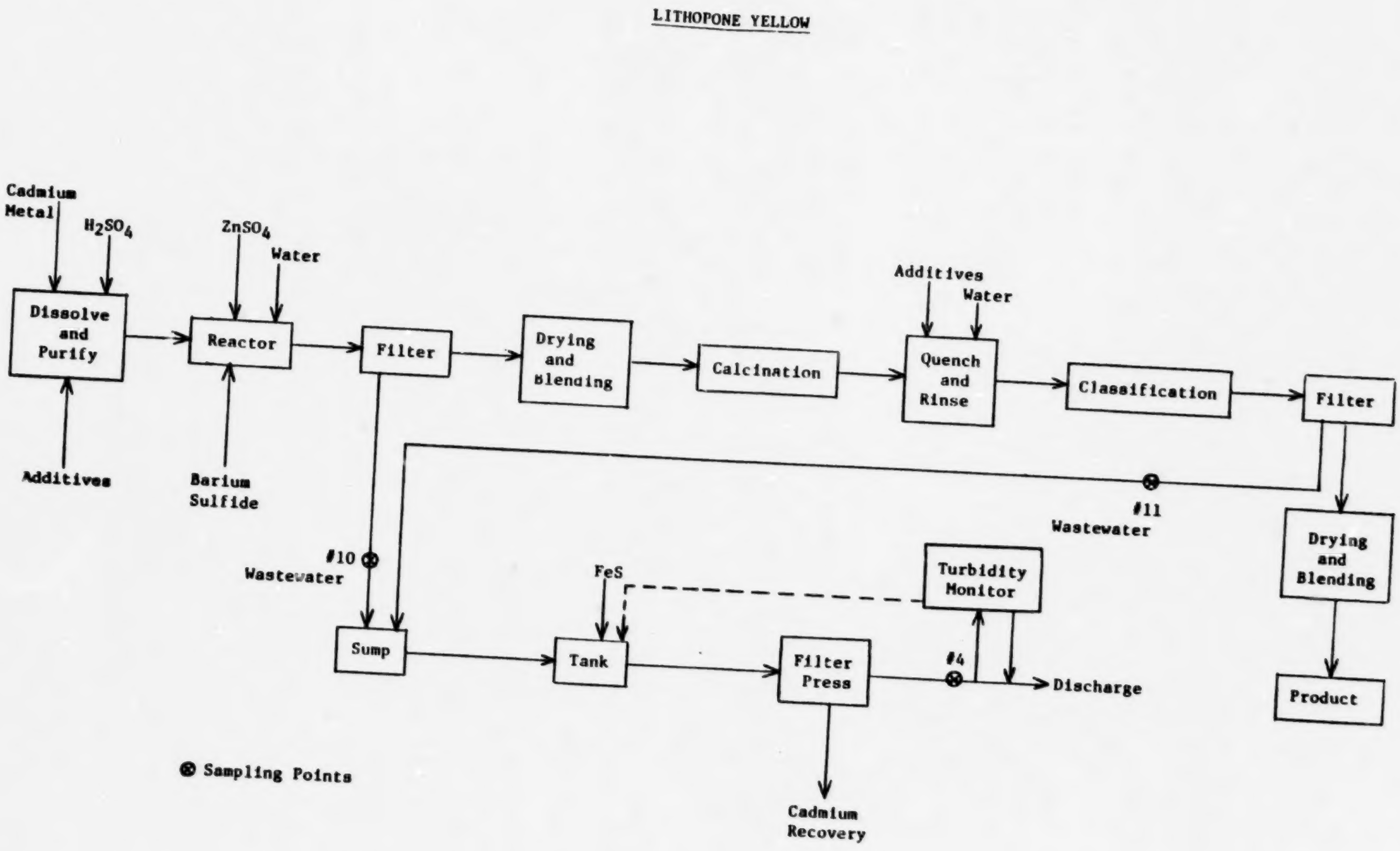

LITHOPONE YELLOW
Cadmium Metal
H2SO4
Dissolve and Purify
Additives
ZnSO4
Water
Reactor
Barium Sulfide
Filter
Drying and Blending
Calcination
Additives
Water
Quench and Rinse
Classification
Filter
#11 Wastewater
Drying and Blending
Product
#10 Wastewater
Sump
FeS
Tank
Filter Press
Cadmium Recovery
Turbidity Monitor
#4
Discharge
⊗ Sampling Points

FIGURE 11-6. PROCESS, WASTEWATER TREATMENT, AND SAMPLING LOCATIONS FOR PLANT F134.

with process wastewater from all other parts of the plant. The 90 percent of the wastewater from the non-cadmium pigment products and the filtrate from cadmium recovery filter press were treated with caustic and then clarified in a clarifier. The effluent from the clarifier, and the effluent from the cadmium treatment plant were then filtered through a sand filter. The filtrate was discharged to a publicly owned treatment works (POTW), and the backwash recycled to the clarifier. The underflow from the clarifier was dewatered and disposed as hazardous wastes and the water recycled for more treatment.

In 1983 the treatment facility was again changed to eliminate the use of the cadmium recovery system. All cadmium pigments process wastewater is now combined with the non-cadmium pigments process wastewater for combined treatment, consisting of hexavalent chromium reduction in acidic solution (the hexavalent chromium is from non-cadmium pigments wastewater) followed by pH adjustment to basic conditions, clarification, and filtration through a sand filter.

During the sampling period, only pure cadmium red pigments were being produced. Figure 11-3 shows wastewater sources from the various processes at Plant F102 and the sample points, in addition to the cadmium recovery treatment system, with its sample points. Table 11-6 gives the pollutant concentrations and unit loadings of pollutants for the sampled streams.

Plant F134 produces both red and yellow cadmium pigments in both the pure and lithopone forms, by the processes shown in Figures 11-4, 11-5 and 11-6, which are similar to the general processes described previously.

Process wastewater and treatment for each color (red and yellow) are similarly segregated. Process wastewater originates from both the primary filter presses (greencake) and the finishing filter presses during loading/pressing and washing operations. For the cadmium lithopone pigments (red and yellow), only the two filter press operations generate wastewater. For the pure cadmium pigments an additional washing period was utilized to wash out impurities, which created an additional wastewater flow.

Ferrous sulfide is added to the wastewater in a floor sump where wastewater is collected, and the wastewater is then pumped to a large holding tank. The resulting precipitate/slurry material is pumped to a final scavenger filter press. The filtrate represents the final effluent which is discharged directly, while the recovered filtercake is sold as a by-product. A continuous turbidity monitoring system permits wastewater to be returned to treatment if certain turbidity levels are exceeded. Process

TABLE 11-6. POLLUTANT CONCENTRATIONS AND LOADS OF THE SAMPLED WASTE STREAMS FOR PLANT F102 CADMIUM PIGMENTS(1)

Stream Number	Stream Description	TSS	Cd	Se	Zn	Pb	Sb
		mg/l kg/kkg					
2	Decant Water Discharge (2 days)	352. 9.22	2083. 54.5	2.67 0.0699	0.12 0.00314	1.1 0.0288	0.72 0.0188
3	Floor Washings & Maintenance Hosedown From Upstairs	740. 0.435	116.6 0.0685	2.29 0.00135	2.5 0.00147	0.34 0.00020	0.11 0.00006
4	Filter Wash	116. 1.799	27.8 0.431	<3.14 <0.0487	2.71 0.0420	1.1 0.0171	1.43 0.0222
5	Wet Scrubber Discharge (1 day)	4.5 0.00242	4.6 0.00247	0.11 0.00006	0.24 0.00013	0.12 0.00006	0.008 0.000004
6	Hot Water Tank Excess Discharge (1 day)	<1.0 <0.0010	0.073 0.00008	<0.005 <0.000005	0.006 0.000006	0.002 0.000002	0.007 0.000007
7	Total Combined Raw Waste	3047. 140.1	1040 47.8	29.7 1.366	25.1 1.154	0.25 0.0115	0.19 0.00874
8	Treated Effluent	189. 8.08	92.0 3.93	0.19 0.00813	0.26 0.0111	0.18 0.00770	0.21 0.00898

(1) Concentrations and loads are average values obtained during three days of sampling (except where noted).

TABLE 11-7. POLLUTANT CONCENTRATIONS AND LOADS OF THE SAMPLED WASTE STREAMS FOR PLANT F134 CADMIUM PIGMENTS(1)

Stream Number	Stream Description	mg/l kg/kkg					
		TSS	Cd	Se	Zn	Pb	Sb
(Pure Yellow)							
2	Greencake Press Washwater (Finisher)	15.0 1.38	0.26 0.0240	0.34 0.0313	0.09 0.00829	0.12 0.0111	0.18 0.0166
3	Greencake Load/Press Water	75.0 0.953	1.9 0.0241	1.2 0.0152	0.74 0.00940	0.58 0.00737	1.90 0.0241
4	Scavenger/Effluent Press Water (Treated)	10.0 1.24	0.11 0.0136	0.11 0.0136	0.027 0.00333	0.12 0.0148	0.33 0.0407
(Lithopone Red)							
5	Greencake Press Water	17.5 0.0914	4.0 0.0209	5.6 0.0292	0.086 0.00045	0.059 0.00031	0.28 0.00146
6	Finishing Press Water	81.3 0.212	8.23 0.0215	0.76 0.00198	<0.004 <0.00001	0.086 0.00022	0.18 0.00047
7	Scavenger/Effluent Press Water (Treated)	8.8 0.0796	0.41 0.00371	3.12 0.0282	<0.026 <0.00024	<0.078 <0.00071	0.20 0.00181
(Lithopone Yellow)							
10	Greencake Press Water	5.0 0.0220	0.61 0.00268	0.0028 0.00001	0.825 0.00362	0.06 0.00026	0.35 0.00154
11	Finishing Press Water	70.0 0.381	15.5 0.0845	0.0058 0.00003	2.65 0.0144	0.077 0.00042	0.20 0.00109
4	Scavenger/Effluent Press Water (Treated)	<5.0 <0.098	0.13 0.00254	0.010 0.00020	0.069 0.00135	0.15 0.00293	0.10 0.00195

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(1) Concentrations and loads are batch flow-proportioned and are average values obtained during three day visit.

wastewater sources and treatment system along with the corresponding sampling points for each pigment product are shown in Figures 11-4, 11-5 and 11-6.

Two visits to plant F134 resulted in separate wastewater and treated effluent samples from the pure cadmium yellow pigment and lithopone cadmium yellow pigment, as well as from the lithopone cadmium red pigment operations.

Table 11-7 presents the wastewater flow and pollutant concentrations for each type of pigment.

Other Plants Visited

Six plants producing cadmium pigments and/or salts were visited during the program period, but not sampled. A description of the individual products and treatment facilities for those plants visited is given in the discussion below.

Plant F101 manufactures cadmium sulfate and cadmium pigments. At present there is no wastewater treatment facility at this plant for treatment of process wastewater. All process wastewaters are discharged to a POTW. Plant personnel are investigating several alternatives to reduce or eliminate the discharge of process water pollutants. One alternative is the use of soda ash neutralization to treat the effluent from the pigment quenching operation. The neutralized effluent would be discharged, and the cadmium carbonate precipitate would be recovered and recycled. A second alternative consists of recycling the quenching effluent directly. This second alternative has not been demonstrated, and some technical problems including safe handling of the hydrogen sulfide gas that could be evolved during recycling, may be difficult to solve.

Plant F128 manufactures cadmium sulfate, cadmium nitrate and cadmium pigments, as well as other chemical products. All of the cadmium pigment plant wastewater except that emanating from the drying operations and air scrubbers is discharged to an in-plant receiver. The wastewater is treated with alkali and then filtered. The filter cake is either sold for recovery of cadmium or disposed of in a chemical waste landfill. The effluent from cadmium treatment joins the wastewater from the drying operations and air scrubbers in a separate in-plant receiver. The receiver carries the wastewaters generated from the rest of the plant processes, as well as the above-mentioned treated cadmium wastewater, to the main wastewater treatment facility. The wastewater is neutralized with lime, settled and filtered in a dual-media filter before discharge to surface waters. The sludge from settling is filtered in a filter press and the filter cake is disposed of in a chemical landfill. The filtrate is recycled to the wastewater treatment facility, as is the backwash wastewater from the periodic backwashing of the dual-media filter.

Plant F117 manufactures cadmium sulfate and cadmium chloride as well as a variety of other metal salts. Process wastewater from cadmium salts production are treated separately. These are very small flows consisting of leaks, spills and washups. Treatment consists of the addition of caustic (NaOH) to the collection sump until the pH is around 10. The sump is then pumped out through a small filter press, and the filtrate is discharged directly to surface waters. The residue is sent to solids disposal.

Plant F107 manufactures cadmium nitrate and a variety of other metal salts. There is no treatment facility at this plant and all wastewaters are discharged to a POTW.

Plant F119 manufactures cadmium nitrate and a variety of other metal salts. All process wastewater from production of metal products undergo combined treatment. This consists of neutralization tanks where pH is adjusted to 8.7 - 9.0 with caustic. The neutralized waste is sent to a settling basin for settling. The settled wastewater is then sent to a flash mix tank where flocculating agents are added and then on to a tube settler for additional solids removal. The overflow discharges to a municipal treatment plant while the underflow goes to a sludge holding tank where it then undergoes filtering in a filter press and disposal in a chemical landfill. Supernatant and filtrate from sludge handling is recycled to the treatment facility.

Plant F145 manufactures cadmium chloride and a variety of other inorganic and organic compounds. All process wastewaters from the entire plant which cannot be recycled are sent to the combined plant wastewater treatment facility. Here the waste is equalized, neutralized with lime slurry to pH 9.5 - 10.2, agitated, and settled in clarifiers. The overflow from the clarifiers is sent to the organics removal portion of the WWTF where it receives biological treatment and is discharged directly to surface waters. Sludge is dewatered and disposed of as solid waste.

Toxic Pollutant Concentrations

Thirteen toxic pollutants were found at detectable concentrations in the raw wastewater at the two sampled plants. The maximum concentrations observed are given in the table below.

TABLE 11-8. TOXIC POLLUTANT RAW WASTE DATA-CADMIUM PIGMENTS

Average Daily Pollutant Concentrations and Loads

$$\frac{\text{mg/l}}{\text{kg/kkg}}$$

	Plant Designation				
Pollutant	(PR) F102(1)	(PY) F134(2)	(LR) F134(2)	(LY) F134(2)	Overall Average
Antimony	0.19 0.00874	0.54 0.0566	0.225 0.00176	0.24 0.00237	0.30 0.0174
Cadmium	1040.0 47.8	0.49 0.0514	6.76 0.0530	11.14 0.110	264.6 12.0
Thallium	0.14 0.00644	0.064 0.0067	0.003 0.00002	0.002 0.00002	0.052 0.00330
Selenium	29.7 1.37	0.26 0.00273	2.0 0.0157	0.005 0.00005	7.99 0.347
Zinc	25.1 1.154	0.20 0.0210	0.035 0.00027	2.12 0.0209	6.86 0.299
Lead	0.25 0.0115	0.3 0.0315	0.081 0.00063	0.072 0.0071	0.18 0.0127
Nickel	0.18 0.00828	0.15 0.0157	0.008 0.00006	0.0072 0.00007	0.086 0.00603
Copper	0.097 0.00446	0.061 0.00640	0.026 0.00020	0.015 0.00015	0.05 0.00280

(1) Data from three 24-hour composite samples, averaged, from the combined total raw waste sampling point.

(2) Data from three days of composite samples collected from individual batches, flow proportioned from each raw waste stream for that particular day and then averaged over the three days.

(PR) Pure Red Pigments.

(PY) Pure Yellow Pigments.

(LR) Lithopone Red Pigments.

(LY) Lithopone Yellow Pigments.

TABLE 11-9. TOXIC POLLUTANT TREATED EFFLUENT DATA CADMIUM PIGMENTS

Average Daily Pollutant Concentrations and Loads

$\frac{mg/l}{kg/kkg}$

	Plant Designation				
Pollutant	(PR) F102(1)	(PY) F134(2)	(LR) F134(2)	(LY) F134(2)	Overall Average
Antimony	0.21 0.00898	0.33 0.0407	0.2 0.00181	0.1 0.00195	0.21 0.0134
Cadmium	92.0 3.93	0.106 0.0131	0.41 0.00371	0.13 0.00254	23.2 0.987
Thallium	0.21 0.00898	0.047 0.00580	0.001 0.00001	0.001 0.00002	0.065 0.00370
Selenium	0.19 0.00813	0.11 0.0136	3.12 0.0282	0.01 0.00020	0.86 0.0125
Zinc	0.26 0.00111	0.027 0.00333	<0.026 <0.00024	0.069 0.00135	<0.095 <0.00151
Lead	0.18 0.0077	0.115 0.0142	<0.078 <0.00071	0.15 0.00293	<0.13 <0.00640
Nickel	0.23 0.00984	0.056 0.00691	0.0086 0.00008	0.014 0.00027	0.077 0.00430
Copper	0.29 0.0124	0.027 0.00333	0.016 0.00014	0.01 0.00020	0.085 0.00327

(1) Data from three 24-hour composite samples, averaged.

(2) Data from composite samples collected from individual batches over three days and averaged.

(PR) Pure Red Pigment.

(PY) Pure Yellow Pigment.

(LR) Lithopone Red Pigment.

(LY) Lithopone Yellow Pigment.

Pollutant	Maximum Concentration Observed (ug/l)
Antimony	540
Arsenic	190
Cadmium	1,400,000
Chromium	400
Copper	250
Lead	530
Nickel	420
Selenium	81,000
Thallium	190
Zinc	62,000
Bis(2-chloroethyl) ether	84
Bis (2-ethyhexyl) phthalate	24.4
Chloroform	40.3
Methylene chloride	14.8

Data was obtained at Plants F102 (one type of cadmium pigment) and F134 (three different cadmium pigments). The organic compounds bis(2-ethylhexyl) phthalate and chloroform were present in high concentrations in the supply water at one plant. In addition, phthalates and methylene chloride are generally found at this concentration as a result of sample contamination from the plasticizers in tubing and laboratory glassware cleaning procedures.

Section 5 of this report describes the methodology of the sampling program. In the cadmium pigments industry, nine days of sampling were conducted at Plants F102 and F134. This involved 15 different sampling points for raw and treated wastewater streams. The evaluation of toxic metals content of these process-related wastewater streams was based on 507 analytical data points. Sampling for organic pollutants generated another 1,824 data points.

In Table 11-8, the toxic pollutant raw wastewater data from the sampling program are presented as the average daily concentrations and unit loadings found at the individual plants and pigment processes. The overall averages were calculated and shown also to present a situation as if a single plant were making all four types of pigments at the same time and they combined the wastes into one raw wastewater stream which could occur at the four discharging plants. The toxic pollutant concentrations and unit loadings in the treated effluents from the sampling program are presented in Table 11-9 for the four pigment types sampled.

POLLUTION ABATEMENT OPTIONS

Toxic Pollutants of Concern

The toxic pollutants found in significant amounts are the heavy metal components of the raw materials and product, as well as the impurities found in the raw materials. The primary pollutant is cadmium, which is present throughout the process train. Selenium and zinc are the second most abundant pollutants and of course depend on which pigment (red or yellow) is being produced. Since all plants produce both pigments, both of these metals would be present in significant amounts at all plants.

The other toxic metals of concern found were lead, antimony, copper, nickel and thallium. These are present in trace amounts due to impurities in the raw materials and subsequently removed during processing of the cadmium pigments. The presence or absence of these five trace metals at significant levels in the wastewater may depend mainly on the levels present as impurities in the materials as well as the degree of purification of the materials to remove them. The fact that these metals are found in such small concentrations could present problems in monitoring due to analytical variability. For example, one plant exhibited higher concentrations of some of these metals in the treated effluent than were found in the raw wastewater.

All the process contact wastewater generated in the cadmium pigments subcategory contain dissolved cadmium and pigment particulates.

Existing Control and Treatment Practices

A description of the individual treatment facilities for those plants visited was given previously. In addition, the following information was obtained for the remaining plants.

Plant F110 manufactures the basic cadmium sulfide pigment. The process wastewater from this plant is sent to the plant treatment facility where it is neutralized with lime to pH 12. The wastewater is then sent to a lagoon for settling. The solids are dredged to the sides of the lagoon and there is no discharge of wastewater from the lagoon. The plant is located in an arid region of the country.

Plant F125 manufactures cadmium nitrate and other metal salts. Wastewaters from the cadmium process are combined with the other product process wastes and treated together. Treatment consists of equalization, sedimentation, pH adjustment with NaOH, and a series of lined and unlined impoundments before discharge to surface waters.

Plant No. F123 produces small quanities of cadmium chloride. This plant discharges no wastewater. All process wastewater is incorporated in the product.

Plant F124 produces cadmium nitrate as well as other metal salts. Treatment of wastewaters for the entire plant consists of alkaline precipitation, clarification, filter press filtration, multi-media filtration, pH adjustment and sedimentation in ponds before discharging directly to surface waters.

Other Applicable Control and Treatment Technologies

Cadmium pigment plants commonly have a cadmium recovery system which uses alkaline or ferrous sulfide precipitation followed by settling and/or filtration. Effluent from the recovery systems still contains considerable amounts of cadmium and further treatment should be applied before discharge. Further treatment by lime precipitation and clarification, followed by sand or dual-media filtration would remove more residual cadmium.

Process Modifications and Technology Transfer Options

One cadmium pigment manufacturer employs a continuous turbidity monitor as part of the wastewater treatment system. The monitoring device is located downstream of a cadmium scavenger filter press and upstream of the final treated discharge. Wastewater not meeting turbidity standards is automatically pumped back to treatment and again sent through the filter press. This offers the advantage of reducing the variations in performance of treatment and aids in control of suspended solids. Control of suspended solids at pigment facilities is essential to reduction of effluent concentrations of cadmium, selenium, and zinc in the final discharge.

Several cadmium pigment producers practice segregation of process wastewater from other products manufactured to enable recovery of cadmium-containing solids. Typically, cadmium-containing wastewater streams are segregated for wastewater treatment/solids recovery, and sludges obtained are sold for recovery of metal values. Treated wastewater is then either discharged or commingled with other wastewater streams for further treatment. In the case of POTW dischargers, much cadmium, selenium, and zinc can be prevented from accumulating in POTW - generated sludges by using wastewater stream segregation and recovery technology.

The use of filter aids to improve filter performance is commonplace in inorganic chemicals manufacturing processes. Transfer of this technology to wastewater treatment processes may facilitate decreasing suspended solids concentrations in wastewater treatment filtrates. The identification and use of effective flocculants and other settling aids could contribute significantly toward enhancing effluent quality in this subcategory.

An overall reduction in water use at cadmium pigments facilities might be obtained by the following approaches:

1. Recycle of filter washwater during pigment finishing process, where possible;
2. Use of noncontact cooling water for make-up water in the salt and pigment process (this would reduce overall water use, but not pollutant discharges);
3. Limit excessive usage of washwater and other process wastewater, where possible;
4. Recycle of scrubber wastewater where possible.

As shown on Tables 11-3 and 11-5, the major water use by far at cadmium pigments plants is direct and indirect process contact wastewater resulting from cleaning impurities from the crude pigments. This cleaning is necessary to produce a saleable product, and the amount of water used for cleaning depends upon the product, the amount of impurity, and the demands of the customer. Therefore, while the above suggestions may save water at those plants that can implement them, no specific technology was identified which could be applied at all plants and result in a significant reduction in the amount of wastewater discharged to treatment.

Best Management Practices

If contact is possible with leakage, spillage of raw materials or product, all storm water and plant site runoff should be collected and directed to the plant treatment facility. This contamination can be minimized by indoor storage of chemicals, proper air pollution control, and development of an effective spill prevention and control program.

All other contact wastewater including leaks, spills, and washdowns should be contained and treated because this practice may enhance recovery of raw materials and product.

If solids from the wastewater treatment plant are hazardous and disposed or stored on-site, provision must be made to control leachates and permeates. Leachates and permeates which contain toxic pollutants should be directed to the treatment system for further treatment.

Advanced Treatment Technology

Cadmium pigments wastewater contains fugitive pigment particles which in turn contain significant concentrations of cadmium, selenium and zinc. Low concentrations of suspended solids must be achieved to ensure reduction of these toxic metals in wastewater discharges. Level 1 plus Level 2 technology will be required as a minimum to achieve these low concentrations. The effectiveness of these technologies can be enhanced by addition of flocculating agents prior to clarification and by the use of sand or multi-media filtration (as opposed to filter press filtration) for Level 2. To illustrate the above, plant F128 practices cadmium recovery followed by further treatment consisting of pH adjustment, clarification, and sand filtration to achieve an average cadmium concentration of 0.07 mg/l.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1

Level 1 treatment consists of alkaline precipitation, clarification or settling, and final pH adjustment of the effluent if necessary. Sludges generated are dewatered in a filter press or collected and disposed of in a hazardous waste landfill. As part of the treatment system, a holding basin sized to retain 4-6 hours of influent is provided as a safeguard in the event of treatment system shutdown. The treatment technology is illustrated in Figure 10-10.

The initial treatment step is the addition of caustic soda. This is followed by clarification/settling (if the wastewater characteristics are suitable, a tube settler may be substituted for a clarifier to conserve space). Sludge is removed from the clarifier and directed to a filter press for dewatering. Pits are provided at the filter press for the temporary storage of sludge. The sludge is periodically transported to a hazardous material landfill. Filter press filtrate is returned to the head of the treatment system.

The pH of the treated wastewater stream is adjusted to an acceptable level by acid addition prior to discharge if necessary. A monitoring system is installed at the discharge point. The objective of Level 1 technology is to remove heavy metals and suspended solids.

Level 1 treatment was not selected as the basis for BPT because it provides inadequate removal of fine suspended cadmium hydroxide particles. Currently, only three facilities still employ Level 1 treatment alone.

B. Level 2

Level 2 treatment consists of granular media filtration of the Level 1 effluent for further removal of cadmium hydroxide precipitates and other solids from the wastewater. This technology is portrayed in Figure 10-11. In practice, when Level 2 technology is added to Level 1, final pH adjustment would be reconfigured to occur after filtration not prior to it. The objective of Level 2 treatment technology in this subcategory is to achieve, at a reasonable cost, more effective removal of toxic metals than provided by Level 1. Filtration will both increase treatment system solids removal and decrease the variation in solids removal exhibited by typical clarifier performance.

Level 2 treatment was selected as the basis for BPT because it represents a typical and viable industry practice for the control of suspended solids, cadmium, zinc and selenium. Currently seven of twelve plants in this subcategory have Level 2 or equivalent treatment technology. Four of the six direct dischargers have Level 2 treatment already installed. Two plants have no discharge and would not incur additional costs.

Equipment for Different Treatment Levels

A. Equipment functions

Conventional sludge dewatering by a filter press is used for sludge removed by the clarification/settling system. In the cadmium pigments segment, this sludge has value and may be recovered. The sludge from the filter press is either disposed of off-site in a hazardous material landfill or sent to an off-site cadmium reclaiming/recovery operation. If a tube settler is used, backwash from the settler as well as from the granular-media filters is returned to the influent holding basin. All equipment is conventional and readily available.

B. Chemical Handling

Caustic soda (50 percent NaOH) is used to precipitate heavy metals in Level 1. Sulfuric acid (concentrated) may be used to reduce the pH of the wastewater prior to discharge.

C. Solids Handling

Treatment sludges for cadmium pigments generated by Level 1 are dewatered in a filter press. The solids may be disposed of off-site in a hazardous material landfill or sent to an off-site cadmium reclaiming/recovery operation. Level 2 filter backwash may be sent to the head of the plant or, if the solids concentration is sufficiently high, may be sent directly to the filter press. Cadmium salts wastewater treatment sludges are not dewatered since the low volume typically produced does not justify the use of a filter press.

Treatment Cost Estimates

In the cadmium pigments and salts subcategory, two model plants were chosen, one representing the cadmium pigments segment and the other representing the cadmium salts segment. In each case, two treatment options were considered. Costs for two model plants were developed because there are significant differences between the production and amounts of wastewater generated even though the wastewaters have similar chemical characteristics.

General

Production ranges and wastewater flow characteristics have been presented earlier in this section and are summarized in Table 11-1. There are six direct dischargers, four indirect dischargers, and two plants which achieve zero discharge.

A. Cadmium Pigments

During development of the model plant characteristics, only data from those facilities which manufacture cadmium pigments were considered. However, since pigment production is universally preceded by manufacture of cadmium salts and since cadmium salts manufacture generates small volumes of wastewater, both sources of wastewater were combined for the purpose of defining model plant characteristics. In fact, most wastewater flow information supplied by industry for pigment plants did not differentiate between wastewater attributable to salts production and to pigments production at those plants.

The model plant production rate of 711 metric tons per year represents the average production for all discharging pigment producers. At proposal, the model plant unit flow of 92.4 cubic meters/metric ton (m^3/kkg) was obtained by computing the average unit flow for the three discharging facilities for which detailed water use information was available (see Table 11-5). Since zero discharge facilities were not included in the computation, the average unit flow value is greater than if zero discharge (zero unit flow) facilities were included. Since proposal, flow and production data for the fourth discharging plant (F128) have been obtained and are shown in Table 11-5. Averaging the unit flows for all four plants results in an average unit flow of 89.2 m^3/kkg, which is an insignificant difference of only three percent. Flow measurements normally are subject to an error greater than three percent. Therefore, the Agency has decided to continue to use 92.4 m^3/kkg as the flow basis for establishing the promulgated limitations, because the differences in actual discharges and cost of treatment would be insignificant if the lower flow (89.2 m^3/kkg) were used. Needless expenditure of resources would be required to revise that number. Most discharging cadmium pigment facilities operate on a 250 day per year basis, so the model plant was also assumed to operate on a similar schedule. The daily discharge volume (262 cubic meters) was derived from the model plant characteristics listed above. These characteristics were used as the basis for treatment cost estimates at all levels.

Material usage for all levels was estimated as follows:

Chemical	Amount	Treatment Level
NaOH (50% sol.)	445 kg/day	1
H_2SO_4 (100%)	52.4 kg/day	1

Total solid waste generated is estimated at 0.18 cubic meters/day for Level 1 and 0.018 cubic meters/day for Level 2. The sludge is assumed to be dewatered to 50% solids by volume.

Model Plant Treatment Costs. On the basis of the model plant specifications and design concepts presented earlier and in Section 10, the estimated costs of treatment for one model with two levels are shown in Table 11-10. The cost of Level 2 is incremental to Level 1.

B. Cadmium Salts

During development of the model plant characteristics, only those facilities producing cadmium salts not destined for production of cadmium pigments were considered salt producers. The model plant for the cadmium salts segment has a production rate of 169 metric tons per year. This figure was obtained by computing the average production for discharging cadmium salt producers. The model plant operating schedule of 150 days per year was based on the average of operating days reported for discharging salt producers. The unit flow value of 0.058 cubic meters/kkg was obtained by computing the average unit flow for those facilities where wastewater flow information was available (see Table 11-4). The daily discharge volume (0.07 cubic meters) was obtained by

TABLE 11-10. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Cadmium Pigments Subgroup

ANNUAL PRODUCTION: 711 METRIC TONS

DAILY FLOW: 262 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2	3	4	5
Facilities	23.0				
Installed Equipment (Including Instrumentation)	168.6	29.4			
Engineering	38.3	5.9			
Contractor Overhead and Profit	34.5	5.3			
Contingency	26.4	4.1			
Land					
Total Invested Capital	290.8	44.7			
Annual Capital Recovery	47.3	7.3			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	112.4	8.9			
Residual Waste Disposal	2.7	0.3			
Total Annual Cost	162.4	16.5			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, sludge dewatering, pH adjustment

LEVEL 2: Filtration

TABLE 11-11. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Cadmium Salts Subgroup

ANNUAL PRODUCTION: 169 METRIC TONS

DAILY FLOW: 0.07 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL				
	1	2	3	4	5
Facilities					
Installed Equipment (Including Instrumentation)	1.9	0.2			
Engineering	0.4	Negl.			
Contractor Overhead and Profit	0.3	Negl.			
Contingency	0.3	Negl.			
Land					
Total Invested Capital	2.9	0.2			
Annual Capital Recovery	0.5	Negl.			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	4.1	0.1			
Residual Waste Disposal	0.1	Negl.			
Total Annual Cost	4.7	0.1			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, pH adjustment

LEVEL 2: Filtration

multiplying daily production by the unit flow value. These data were used as the basis for treatment cost estimates at all levels.

Material usage for both levels was estimated as follows:

Chemical	Amount	Treatment Level
NaOH (50% sol.)	0.12 kg/day	1
H_2SO_4 (100%)	0.014 kg/day	1

Total solid waste generated is estimated at 0.0012 cubic meters/day for Level 1 and 0.001 cubic meters per day as Level 2. The sludge is assumed to contain 2% solids by volume.

Model Plant Treatment Costs. On the basis of model plant specifications and design concepts presented earlier and in Section 10, the estimated costs of treatment for one model with two levels are shown in Table 11-11. The cost of Level 2 is incremental to Level 1.

Basis for Regulations

Basis for BPT Limitations

A. Technology Basis

For BPT, the Agency is proposing limitations based upon alkaline precipitation, clarification, dewatering of the sludge in a filter press, granular media filtration of the clarifier effluent, followed by pH adjustment (if necessary). Currently seven of the twelve plants in this subcategory have this technology or its equivalent installed. Of the six direct dischargers in this subcategory, four have this technology installed. Two additional plants have no discharge and thus would not be affected.

B. Flow Basis

For the cadmium pigments segment, a unit flow rate of 92.4 m^3/kkg was selected as being representative of the group. This flow rate was derived as described above under model plant treatment costs.

For the cadmium salts segment, a unit flow of 0.058 m^3/kkg was selected as being representative of the group. This flow rate was derived as described above under model plant treatment costs.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are being established is based on an evaluation of the raw wastewater data from screening and verification, consideration of the raw materials used in the process, literature data, historical discharge monitoring reports and permit applications, and the treatability of the toxic pollutants.

Tables 8-1 through 8-14 summarize the achievable concentrations of toxic metal pollutants from the literature using available technology options, other industries, and treatability studies. Water use and discharge data are presented earlier in Section 11 together with generalized process characteristics. Pollutant concentrations of raw wastewater streams and a summary of maximum concentrations observed of toxic pollutants detected during screening and verification sampling at several plants are also presented earlier in this section. Data from Appendix A on the performance of in-place industry treatment systems was also utilized in developing the list of pollutants to be regulated.

Based upon the occurrence of treatable levels of specific toxic metals, cadmium, lead, selenium, and zinc were selected as candidate toxic pollutants for BPT regulations. Antimony, arsenic, chromium, copper, mercury, nickel, silver, and thallium were detected but at less than treatable levels.

Consideration of the raw wastewater concentrations presented earlier, industry data, and information in Section 8 related to the effectiveness of hydroxide precipitation, clarification and filtration leads to the selection of cadmium, selenium, and zinc as toxic pollutants to be regulated. As discussed in Section 8, proper control of zinc concentrations will also achieve control of lead, so that lead was not selected for regulation.

D. Statistical Analysis of Influent and Effluent Data for Cadmium Pigments

The proposed effluent limitations for the Cadmium Pigments subcategory were based upon treatment consisting of alkaline precipitation, clarification, and granular media filtration. The proposed effluent limitations for cadmium and zinc were based on effluent data from Plant F128.

Industry comments on the proposed regulation suggested that the limitations were too stringent because the cadmium pigments process wastewater at Plant F128, which produces other inorganic chemical products and combines the wastewater for treatment, comprises only three percent of the total flow of wastewater to treatment. The industry contended that the cadmium levels in the raw waste were diluted and consequently the effluent levels were abnormally low. Industry also commented that only some cadmium pigments contained zinc and that the zinc level in raw waste would be higher when producing those pigments than it would be otherwise. To address these issues, EPA utilized data submitted during the comment period from Plant F128, which submitted both influent and effluent data, and Plant F102, which submitted effluent data with only a limited amount of influent data.

Analysis of Cadmium Data

Analytical Plan

1.) In order to address the question of the effect of dilution, a correlation analysis was performed comparing influent and effluent data sets at Plant F128. This analysis was performed to determine whether or not a more dilute influent stream would be associated with lower effluent cadmium concentrations provided the same treatment technology were applied.

2.) If a strong positive correlation were found by the above analysis it was determined that the Plant F128 data would be screened to remove all effluent cadmium values associated with low levels of influent cadmium. The screening level would be determined on the basis of the limited influent cadmium data available from Plant F102. In this way it was hoped that the resulting influent data set would be comparable to the available Plant F102 influent data set. That is, the effect of the greater dilution at Plant F128 would be eliminated. The resulting Plant F128 influent data set would be compared statistically with the Plant F102 influent data set to determine whether the two are equivalent. If no correlation were found (or if a negative correlation were indicated), the commenter's contention would be judged to be unfounded and no change would be made to the proposed limitations.

3.) If the influent data sets were comparable, then the screened effluent data set from Plant F128 would be analyzed to determine long-term average and variability factors using the methods described in Section 8.

4.) The Plant F102 effluent cadmium data would also be analyzed according to the methodology described below. However, the data would first be screened to remove data associated with non-compliance with chromium pigments guidelines (see discussion below).

5.) The screened effluent data sets from Plants F128 and F102 would be compared statistically to determine whether they are also comparable. This analysis would address the question of conflict between chromium removal and cadmium removal requirements.

Statistical Methods

Mann-Whitney U-test

The Mann-Whitney U-test, also known as the Wilcoxon test, is a nonparametric method for testing the hypothesis that two populations of data are identical on the basis of sample data sets taken from these populations. This test is based upon a rank ordering of the data and is independent of the shape of the data distribution. A complete discussion of this test can be found in Reference 4. The formulae used are:

$$U = n_1 n_2 + \frac{n_1(n_1 + 1)}{2} - R_1$$

where n_1 and n_2 are the numbers of data in each sample set and R_1 is the sum of the ranks in the first sample set.

$$E(U) = \frac{n_1 n_2}{2}$$

$$\mathrm{var}\ (U) = \frac{n_1 n_2 (n_1 + n_2 + 1)}{12}$$

$$Z = \frac{U - E(U)}{\mathrm{var}(U)}$$

where E(U) is the expected value of U and var (U) is the variance of U. If $|Z|$ is greater than 1.96 then the populations are judged to be different at the 5% significance level.

Spearman's Rho

Spearman's rank order correlation is a method for determining whether two paired data sets are related. This analysis is based upon a rank-ordering of the two data sets and the subsequent comparison of the ranks of the corresponding elements of each set. Rho, the correlation coefficient computed, can range from -1 to +1. Values close to -1 or +1 indicate strong relationships, while values close to zero indicate weak relationships. This method, since it is based upon the rank orders rather than the data themselves, is independent of the shapes of the data distributions. A complete description of the computational procedure involved can be found in Reference 5. The formulae used are:

$$\text{rho} = 1 - \frac{6\ \Sigma D^2}{N(N^2 - 1)}$$

where D is the difference between the ranks of a given data pair and N is the number of data pairs.

The significance of the rho value calculated is determined on the basis of a Z-test. That is,

$$Z = N - 1$$

If $|Z|$ is greater than 1.96, then rho is significant at the 0.05 level.

DATA ANALYSIS RESULTS

A rank order correlation was performed in order to assess the relationship between influent and effluent cadmium concentrations at Plant F128. Data used omitted only those data having discrepancies in reported flows. This was done since the effluent cadmium data were reported as loadings and thus required conversions dependent on the flow in order to arrive at concentration values. Eight data points were omitted due to flow reporting discrepancies. For this analysis there remained 141 data pairs. A positive correlation coefficient (Spearman's Rho) of 0.65 was obtained having a Z value of 7.68. The correlation coefficient of 0.65 indicates a level of relationship between influent and effluent cadmium concentrations which would occur by chance less than 1 time in 100, given the 141 data points available.

The correlation coefficient of 0.65 suggests that when influent cadmium concentrations are higher, the resulting effluent concentrations will be higher given the same treatment system. This result might be extrapolated to suggest that if two facilites have comparable treatment systems in place, the plant having the greater influent concentrations of cadmium would not be expected to achieve the same effluent level as its counterpart with the lower influent concentrations. This analysis addresses the comment questioning the use of long-term average concentrations at a plant whose influent cadmium concentration is diluted by other waste streams. Since there is apparently a relationship between influent and effluent concentrations of cadmium, the Plant F128 data were screened to minimize the effluent of low influent cadmium concentrations on the calculated long-term average.

Many of the influent samples at Plant F128 were quite low in total cadmium content as compared with the Plant F102 influent data. In order to use the data submitted by F128 as a predictor of achievable effluent cadmium concentrations, the data were screened to remove all data points corresponding to influent levels less than 1.2 mg/l. 1.2 mg/l was selected as the screening level since this was the lowest influent total cadmium concentration reported in the data from Plant F102, excluding the first two days, which were judged to be non-representative due to start-up conditions.

In addition to the differences at the low ends of their influent cadmium concentration ranges, the maximum value reported by F128 was 19 mg/l while the maximum value reported by F102 was 43.8 mg/l. The average influent concentration at F102 was 10 mg/l while after screening the F128 data, the average concentration was 4 mg/l. Therefore, following the data screening, a Mann-Whitney U-test was performed to determine whether the influent data at F102 were comparable to the screened influent data from F128. The result of this analysis was that the two data sets are equivalent at the 5% level ($Z = 1.22$). This is interpreted to mean that the screened influent data at F128 are comparable to the influent data at F102. On the basis of the earlier correlation analysis, the effluent concentrations would be expected to be similar if equivalent treatment were practiced.

On the basis of the above results, and the technical judgement that F128 achieves good operational control in its wastewater treatment system, the effluent data corresponding to the screened influent data set were analyzed to determine a long-term average and variability factors. These results are summarized below:

F128 Screened Effluent Cadmium Data (All data excluded where influent total Cd<1.2 mg/l)

Number of data points	39
Mean	0.14 mg/l
Standard Deviation	0.14 mg/l
Range	0.025 to 0.77 mg/l
Variability Factor (24-hr. max.)	5.09
Variability Factor (30-day avg.)	1.31

The treatment technology upon which the chromium pigments guidelines were established includes SO_2 reduction of Cr^{+6} to Cr^{+3}, alkaline precipitation at about pH = 8.5, clarification, and filtration. For cadmium pigments, alkaline precipitation is recommended at about pH = 10.5, followed by clarification and filtration. Control of pH is critical in order to maintain total chromium discharge levels within the effluent guidelines. pH control is equally critical for cadmium discharge limits, while the two metals follow different solubility trends around the control point (about pH - 9-10). Therefore screening was applied to the data in order to avoid selecting a cadmium discharge level which in effect forces chromium non-compliance. The F128 data set contained only one data point which had an effluent chromium concentration above 2.9 mg/l (the maximum chromium effluent limitation in the chrcmium pigments guideline). This value was 3.0 mg/l (i.e. 3% over the maximum limitation). However, this point had been screened out due to low influent cadmium concentration.

In addition, effluent cadmium data from F102 were analyzed according to the methodology described in Section 8. Data were first screened to remove all data corresponding to poor treatment.

Fifty data points had been identified for exclusion by Plant F102 because of treatment system upset conditions. Consequently these data were not included. Further screening was based upon concentrations of chromium and TSS, which are subject to the limitations for the chromium pigments subcategory. Effluent cadmium data were omitted which correspond to effluent chromium concentrations greater than 2.9 mg/l or effluent TSS concentrations greater than 87 mg/l. These screening levels were selected since they are the effluent guideline levels for chromium pigments currently in effect. A long-term average and variability factors were computed as summarized below:

F102 Screened Effluent Cadmium Data (All data excluded where effluent Cr<2.9 mg/l or effluent TSS<87 mgl)

Number of data points	130
Mean	0.20 mg/l
Standard Deviation	0.25 mg/l
Range	0.02 to 1.29 mg/l
Variability Factor (24 hr. max.)(1)	5.87
Variability Factor (30-day avg.)(1)	1.37

A secondary screening was performed on the F102 data in order to eliminate instances of low chromium discharge with associated high cadmium levels, which could indicate a pH optimization for chromium removal which could cause high cadmium discharges. Four such data points were identified.

The resulting summary statistics are as follows:

Number of data points	126
Mean	0.18 mg/l

Standard Deviation	0.21 mg/l
Range	0.02 to 1.29 mg/l
Variability Factor (24-hr. max.)	5.64
Variability Factor (30-day avg.)	1.35

These statistics suggest that even after screening the two data sets, F128 achieves superior effluent cadmium reduction. However, a Mann-Whitney U-test was performed to determine whether the apparent differences between the screened effluent data sets at the two plants were statistically significant. The result of this test indicates that the two effluent data sets are equivalent at the 5% level, ($Z = 1.91$). Thus, the apparent differences are attributable to chance.

It should be noted that the data provided by Plant F102 included data from a considerable number of days (50) when wastewater treatment plant upsets had occurred. These data had been identified as non-representative by the company and generally were characterized by extremely high effluent concentrations of one or more control parameter(s).

Summary and Conclusions

On the basis of the statistical analyses described above, the following conclusions can be drawn:

1. There is a positive correlation between influent cadmium concentration and effluent cadmium concentration at Plant F128. This suggests that, while effluent cadmium concentrations are consistently low at this facility, this may be related to lower influent concentrations at this facility as compared with other cadmium pigments production facilities.

2. When the data from F128 are screened to eliminate instances of low influent cadmium concentrations (i.e. lower than F102, the only other plant having provided influent data) creating an influent data set comparable to that of F102, the long-term average effluent cadmium concentration is approximately 0.14 mg/l.

3. When the data from F102 are screened to eliminate instances of poor treatment system control, the effluent data set is comparable statistically to the screened effluent data set from F128, yielding a long-term average cadmium concentration of 0.20 mg/l.

Recommendations

In view of the high effluent cadmium concentrations, frequent high chromium levels, the high variability in cadmium and chromium effluent levels as well as the frequent instances of very poor TSS control, it is apparent that the F102 facility is in need of improved treatment system control. Therefore the data from this facility are not believed to represent the levels achievable by application of BAT/BPT treatment technology to the cadmium pigments subcategory. While the facility employs a sand filtration unit, there have been multiple instances of effluent TSS concentrations greater than 100 mg/l (and frequently in the 500 to 1,000 mg/l range). Also pH control is applied for chromium removal, but frequent occurrences of chromium concentrations greater than 5 and as high as 94.8 mg/l in the plant's treated effluent suggest that the control of this treatment process is inadequate. In view of these facts this plant is not used as a basis for recommended guidelines. However, the results of analysis of screened data from this facility indicate that improved filtration unit operation and improved pH control will substantially improve overall treatment system performance, producing effluent cadmium concentrations similar to those obtained at F128. This improved performance should not require large capital expenditures, since the BAT treatment system unit operations have already been installed. There would most likely be need for smaller expenditures associated with improved control systems and operating and maintenance practices. Costs associated with the necessary control systems have been included in the EPA cost analysis both for capital and annual costs.

On the other hand, F128 exhibits relatively consistent effluent quality. No data from this facility were omitted due to treatment upset conditions. In addition, the screening process employed has apparently eliminated the effect of dilution on the effluent quality. Therefore, we have used a long-term average of 0.14 mg/l for guideline development.

Variability factors, however, should be selected on a different basis. Since both data sets have been truncated either on the high end or the low end of their ranges, the natural variability of the data sets has been compressed, and cannot be used as representative of wastewater treatment system performance at the average plant. Variability factors of 2 and 6 were established for the subcategory on the basis of unscreened historical data for the period 1/79-12/80 at plant F128. These factors were 2 for the 30-day average and 6 for the 24-hour maximum. These data covered a period of time when EPA believes the plant to have been operating normally since economic conditions were generally normal.

Using these factors and the long-term average concentration of 0.14 mg/l yields the following recommended standards:

30-day average Cd concentration = 2 X 0.14 mg/l = 0.28 mg/l

24-hr. maximum Cd concentration = 6 X 0.14 mg/l = 0.84 mg/l

Variability factors calculated from the entire Plant F128 data set (i.e., 1/3/79 through 12/21/83) were not used for guideline development since this time period included several periods of atypically low production due to the economic conditions at the time. These periods are believed by EPA to affect the long-term variability.

Analysis of Zinc Data

Only Plant F128 data were used because Plant F102 submitted only five days of zinc effluent data.

Analytical Plan

1.) In order to address the question of the effect of dilution, a correlation analysis was performed comparing influent and effluent data sets at Plant F128. This analysis was performed in order to determine whether or not a more dilute influent stream would be associated with lower effluent zinc concentrations provided the same treatment technology were applied.

2.) If a strong positive correlation was found it was determined that the F128 data would be screened to remove all effluent zinc values associated with low levels of influent zinc. The screening level would be determined on the basis of an examination of the influent data base to locate a break or other point in the data where it could be judged that zinc-containing pigment (cadmium yellow) production was evidently underway when the influent zinc concentration was above the selected level.

3.) Long-term average and variability factors would be computed according to the methodology described in Section 8.

4.) If a weak relationship were shown between influent and effluent zinc concentrations, the long-term average and variability factors would be calculated for both the screened and unscreened data sets, and a statistical comparison would be made between the screened and unscreened effluent data sets to determine whether or not any apparent differences between the two were statistically significant.

Statistical Methods

The statistical methods used were the same as described above for analysis of the cadmium data.

Results

A rank-order correlation was performed in order to assess the relationship between influent and effluent total zinc concentrations. Data used omitted only those data having discrepancies in reported flows. This was done since the effluent zinc data were reported as loadings and thus required conversions dependent on the flow in order to arrive at concentration values. Eight data points were omitted due to flow reporting discrepancies. For this analysis there remained 142 data pairs. Correlation coefficients range from -1 to +1. Values close to -1 or +1 indicate strong relationships while those close to zero indicate weak relationships. This analysis yielded a correlation coefficient of 0.38 (Spearman's Rho), showing a weak, but statistically significant relationship between influent and effluent zinc concentrations at this plant. Given the number of data pairs available for the analysis (142), this degree of correlation would occur by chance less than one time in 100.

This result was further supported by the subsequent analysis of the effluent data set both with and without screening to remove all instances of low influent zinc concentrations. Low influent zinc concentrations were taken as concentrations below 1.2 mg/l. This level was selected on the basis of an examination of the F128 influent data. There is an apparent break in the data at the 1.2 mg/ level. In addition, it is highly likely that influent concentrations above this level are indicative of cadmium yellow pigment production (See the data for Plant F134 above.) Also, the 1.2 mg/l concentration represents a treatable level of zinc in wastewater. The table below summarizes the results of these analyses:

	Screened Data	Unscreened Data
Number of Observations	46	142
Mean (mg/l)	.06	.05

Standard Deviation (mg/l)	.035	.028
Range (mg/l)	0.005-0.20	0.005-0.20
Coefficient of Variation	.58	.56
Variability Factor (24-hr. max.)	3.05	2.95
Variability Factor (30-day avg.)	1.17	1.17

In order to determine whether the apparently small differences between the screened and unscreened data sets are statistically significant, a Mann-Whitney U-test was performed. The result of this analysis was that the two data sets are judged to be different with a statistical significance at the 5% level (Z = 3.00). That is, these differences would occur by chance less than 5% of the time given the number of data available.

From a treatability standpoint, the means of the screened and unscreened data sets are very nearly the same as are the standard deviations, while the ranges of the data are identical and the coefficients of variation and variability factors are nearly the same.

The similarity of these two data sets may be related to the fact that the influent concentrations of zinc reported are considered to be relatively low and the treatment system appears to be consistently reducing the zinc concentrations in the effluent to levels generally recognized as treatability levels in other industries.

Summary and Conclusions

On the basis of the statistical analyses described above, the following conclusions can be drawn:

1.) There is a weak, but statistically significant relationship between influent and effluent zinc concentrations at Plant F128.

2.) When the data from this plant are screened to eliminate instances of low influent zinc concentrations the resulting data set is different from the unscreened data set with statistical significance at the 5% level.

3.) Actual numerical values for the long-term average and variability factors for the screened and unscreened data sets are very close from a treatability standpoint.

Recommendations

On the basis of these results the long-term average zinc concentration of 0.061 mg/l to establish final effluent zinc guidelines for the cadmium pigments subcategory of the Inorganic Chemicals Point Source Category.

However, we have used the variability factors of 1.67 (30-day avg.) and 3.00 (24-hr. max.) derived from effluent data for the period 1/79-12/80 rather than those calculated here, since it is believed by EPA that the period 1/3/79 through 12/21/83, during which time these data were obtained, includes some atypically low production periods due to economic factors. These periods would certainly influence the variability of the data.

E. Basis of BPT Pollutant Limitations

Limitations are presented as both concentrations (mg/l) and loads (kg/kkg), and the relationship between the two is based on the unit flow rate of 92.4 m^3/kkg for cadmium pigments and 0.058 m^3/kkg for cadmium salts.

BPT limitations, which apply to all process wastewater discharged, are presented in Table 11-12 (Cadmium pigments) and Table 11-13 (Cadmium salts).

1. Conventional Pollutants

a. pH

The treated effluent is to be controlled within the range of 6.0 - 9.0. This limitation is based upon the data presented in Appendix B of the Development Document for Proposed Effluent Guidelines for Phase I Inorganic Chemicals (Ref. 2) and the JRB study (Ref. 3).

b. TSS

The BPT limitations for TSS are based on an average of long-term TSS monitoring data from Plants A and K as presented in Appendix A of the Phase I Development Document which use the same Level 2 (filtration) technology to control TSS that is promulgated for the cadmium pigments and salts subcategory.

Data received from Plant F128 during the comment period shows the plant is achieving the limitations derived below. Therefore, we have not revised this section. A long-term average of 9.3 mg/l (the average of both plants) was used to develop the discharge limitations for plants employing filtration. Variability factors, also obtained from Plants A and K of 1.8 for a monthly average and 3.0 for a 24 hour maximum were used yielding TSS concentration limits of 17 mg/l and 28 mg/l respectively. Thus, utilizing these values, one obtains TSS mass limitations for the cadmium pigments segment of:

30-day average:
(17 mg/l) (92.4 m^3/kkg) (kg/10^6mg) (1000 l/m^3)
= 1.57 kg/kkg

24-hour maximum:
(28 mg/l) (92.4 m^3kg) (kg/10^6 mg) (1000 l/m^3)
= 2.59 kg/kkg

Similarly, for the cadmium salts segment:

30-day average:
(17 mg/l) (0.058 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.001 kg/kkg

24-hour maximum:
(28 mg/l) (0.058 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.0016 kg/kkg

2. Toxic Pollutants

a. Cadmium

The BPT limitations for cadmium are based on long-term monitoring data from Plant F128 as described above and presented in Appendix A. In addition to the data described above, some data is available from Plant F134 which has ferrous sulfide plus filtration technology which is not the same as Level 2 and does not perform as well. Since the plant F134 treatment system does not perform as well as Level 2 treatment, the data from Plant F134 were not used. Variability factors derived from the unscreened data at Plant F128 of 2.0 for a 30-day average and 6.0 for a 24-hour maximum were used yielding cadmium limitations of 0.28 mg/l and 0.84 mg/l respectively. Thus utilizing these values, mass limitations for the cadmium pigments segment are obtained as follows:

30-day average:
(0.28 mg/l)(92.4 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.026 kg/kkg

24-hour maximum:
(0.84 mg/l)(92.4 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.078 kg/kkg

Similarly, for the cadmium salts segment:

30-day average:
(.28 mg/l)(0.058 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.0000162 kg/kkg

24-hour maximum:
(.84 mg/l)(0.058 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.0000487 kg/kkg

b. Selenium

The BPT limitations for selenium are based upon screening and verification sampling at Plant F102 since no plant with a well-operated treatment system could be found with long-term effluent monitoring data for selenium. Plant F102 provided long-term data during the comment period. However, as discussed above, we do not believe it is operating the treatment system optimally. Since cadmium is very toxic, we are concerned that adjustments to the proposed limitations for selenium could upset the control of cadmium. Therefore, we did not use the new effluent data from F102. Screening and verification data from plant F134 were not used because it was not producing pure cadmium reds and had a low selenium raw waste load. Since there is insufficient data to derive reliable variability factors for selenium, the variability factors of 2 for a 30-day average and 6 for a 24-hour maximum from treatment system performance for cadmium from Plant F128 were used yielding selenium limitations of 0.4 and 1.2 mg/l respectively. Thus, utilizing these values, mass limitations computed for cadmium pigments are as follows:

30-day average:
(0.4 mg/l)(92.4 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.037 kg/kkg

TABLE 11-12. BPT EFFLUENT LIMITATIONS FOR CADMIUM PIGMENTS

Conventional Pollutants	Long-Term Avg. (mg/l)	VFR	Conc. Basis (mg/l) 30-day avg.	Conc. Basis (mg/l) 24-hr. max.	Effluent Limit (kg/kkg) 30-day avg.	Effluent Limit (kg/kkg) 24-hr. max.
TSS(4)	9.3(1)	1.8/3.0(1)	17	28	1.57	2.59
Toxic Pollutants						
Cadmium(5)	0.14(2)	2/6(2)	0.28	0.84	0.026	0.078
Selenium(5)	0.2(3)	2/6(2)	0.4	1.2	0.037	0.11
Zinc(5)	0.061(2)	1.67/3.0(2)	0.10	0.18	0.0092	0.017

VFR - Variability Factor Ratio

(1) Based upon long-term data at Plants A and K (Phase I)
(2) Based upon long-term data at Plant F128.
(3) Based upon screen sampling at Plant F102.
(4) Also applicable to NSPS and BCT.
(5) Also applicable to BAT and NSPS.

TABLE 11-13. BPT EFFLUENT LIMITATIONS FOR CADMIUM SALTS

			Conc. Basis (mg/l)		Effluent Limit (kg/kkg)	
Conventional Pollutants	Long-Term Avg.(mg/l)	VFR	30-day avg.	24-hr. max.	30-day avg.	24-hr. max.
TSS(4)	9.3(1)	1.8/3.0(1)	17	28	0.001	0.0016
Toxic Pollutants						
Cadmium(5)	0.14(2)	2/6(2)	0.28	0.84	0.0000162	0.0000487
Selenium(5)	0.2(3)	2/6(2)	0.4	1.2	0.000023	0.000070
Zinc(5)	0.061(2)	1.67/3.0(2)	0.10	0.18	0.0000058	0.0000104

VFR - Variable Factor Ratio (30-day avg./24-hr. max.)

(1) Based upon long-term data at Plants A and K (Phase I).
(2) Based upon long-term data at Plant F128.
(3) Based upon screen sampling at Plant F102.
(4) Also applicable to NSPS and BCT.
(5) Also applicable to BAT and NSPS.

24-hour maximum:
(1.2 mg/l)(92.4 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.11 kg/kkg

Similarly, for cadmium salts:

30-day average:
(0.4 mg/l)(0.058 m^3/kkg) (kg/10^6) .1000 l/m^3)
= 0.000023 kg/kkg

24-hour maximum:
(1.2 mg/l)(0.058 m^3/kkg (kg/10^6 mg) (1000 l/m^3)
= 0.000070 kg/kkg

c. Zinc

The BPT Limitations for zinc are based on long-term monitoring data from Plant F128 presented in Appendix A and as described above. No other long-term monitoring data is available from any other cadmium pigments or cadmium salts plant. Variability factors developed for zinc at that plant were 1.67 for a 30-day average and 3.0 for a 24-hour maximum which yield limitations of 0.10 mg/l and 0.18 mg/l respectively. Utilizing these values, mass limitations for the cadmium pigments segment are obtained as follows:

30-day average:
(0.1 mg/l)(92.4 m^3/kkg (kg/10^6 mg) (1000 l/m^3)
= 0.0092 kg/kkg

24-hour maximum:
(0.18 mg/l)(92.4 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.017 kg/kkg

Similarly, for the cadmium salts segment:

30-day average:
(0.1 mg/l)(0.058 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.0000058 kg/kkg

24-hour maximum:
(0.18 mg/l)(0.058 m^3/kkg) (kg/10^6 mg) (1000 l/m^3)
= 0.0000104 kg/kkg

Basis for BCT Effluent Limitations

TABLE 11-14. BAT EFFLUENT LIMITATIONS FOR CADMIUM PIGMENTS AND SALTS SUBCATEGORY

a. Cadmium Pigments (Flow basis 92.4 m3/kkg)

Toxic Pollutants	L.T.A. (mg/l)	VFR	Concentration (mg/l) 30-day avg.	Concentration (mg/l) 24-hr. max.	Effluent Limitations 30-day avg.	Effluent Limitations 24-hr. max.
Cadmium	0.14	2/6	0.28	0.84	0.026	0.078
Selenium	0.2	2/6	0.4	1.2	0.037	0.11
Zinc	0.061	1.67/3.0	0.10	0.18	0.0092	0.017

b. Cadmium Salts (Flow basis 0.058 m^3/kkg)

Cadmium	0.14	2/6	0.28	0.84	0.0000162	0.0000487
Selenium	0.2	2/6	0.4	1.2	0.000023	0.000070
Zinc	0.061	1.67/3.0	0.10	0.18	0.0000058	0.0000104

L.T.A. = Long-term average achievable level.

VFR = Variability Factor Ratio; ratio of the 30-day average variability factor to the 24-hour maximum variability factor.

On October 29, 1982, EPA proposed a revised BCT methodology. While EPA is considering revising that proposed methodology, in this subcategory no additional technologies were identified which would remove significant additional quantities of conventional pollutants. Accordingly, EPA has determined that BCT equals BPT in this subcategory. As a result, BCT for TSS is equal to the BPT limitations.

Basis for BAT Effluent Limitations

Application of Advanced Level Treatment

For BAT, the Agency is promulgating limitations based on treatment consisting of Level 1 plus Level 2 (BPT) technology. Toxic pollutants limited by the proposed BAT regulation are cadmium, selenium, and zinc at the same concentration levels and loadings promulgated for BPT. No additional technology which would remove significant quantities of additional pollutants is known.

A. Technology Basis

Alkaline precipitation followed by clarification, dewatering of the sludge in a filter press, and filtration of the clarifier effluent followed by pH adjustment (if necessary) used for BPT is the same as for BAT.

B. Flow Basis

A unit wastewater flow rate of 92.4 m^3/kkg of cadmium pigments and 0.058 m^3/kkg of cadmium salts has been selected for BAT (same as BPT).

C. Selection of Pollutants to be Regulated

Toxic Pollutants

The toxic pollutants cadmium, selenium, and zinc have been selected at the same concentration levels and loadings proposed for BPT. Table 11-14 presents the BAT limitations for the Cadmium Pigments and Salts Subcategory.

Basis for NSPS Effluent Limitations

For NSPS, the Agency is promulgating limitations equal to BPT because no additional technology that removes significant quantities of additional pollutants is known. The pollutants limited include pH, TSS, cadmium, selenium, and zinc which are listed in Table 11-12 (cadmium pigments) and Table 11-13 (cadmium salts).

Basis for Pretreatment Standards

The Agency is promulgating PSES and PSNS that are equal to BAT limitations because, as shown below, BAT provides better removal of cadmium, selenium, and zinc than is achieved by a well operated POTW with secondary treatment installed and, therefore, these toxic pollutants would pass through a POTW in the absence of pretreatment. Pollutants regulated under PSES and PSNS are cadmium, selenium, and zinc.

Using the average raw waste data presented in Table 11-8 and the long term average effluent from Table 11-12, the Agency has estimated the percent removals for cadmium, selenium, and zinc by comparing the untreated waste concentrations for those three toxic metals with the treated waste concentrations for the selected BAT technology for those same three pollutants. The calculation is as follows:

Cadmium: Raw Waste = 265 mg/l
BAT = 0.14 mg/l

Percent Removal = [(265-0.14)÷(265)](100)
= 99.94%

Selenium: Raw Waste = 8 mg/l
BAT = 0.2 mg/l

Percent Removal = [(8-0.2)÷(8)](100)
= 97.5%

Zinc: Raw Waste = 6.9 mg/l
BAT = 0.061 mg/l

Percent Removal = [(6.9-0.061)÷(6.9)](100)
= 99.1%

The percent removals are greater than the removals achieved for cadmium (38% removal) and zinc (65% removal) by 25% of the POTWs in the "50 cities study" (*Fate of Priority Pollutants in Publicly Owned Treatment Works*, Final Report, EPA 440/1-82/303, September 1982). Limited information showing the removal of selenium by POTWs is available but the removals by 25% of the POTWs in that study for other toxic metals ranged from 19% to 66%. We presume that selenium removals are in that range because selenium behaves similarly to other toxic metals. Therefore, since the BAT technology achieves a greater percent removal of cadmium, selenium, and zinc than is achieved by a well operated POTW with secondary treatment, those three toxic metals would pass-through the POTW in the absence of pretreatment.

Existing Sources

There are currently four indirect discharger cadmium pigments and salts plants in the subcategory. For Pretreatment Standards for Existing Sources (PSES), the Agency is promulgating limitations based on BAT described above. The pollutants limited are cadmium, selenium, and zinc as presented in Table 11-12 (cadmium pigments) and Table 11-13 (cadmium salts).

New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is setting limitations based on NSPS. Since NSPS is equal to BAT, Table 11-12 (cadmium pigments) and Table 11-13 (cadmium salts) summarize the limitations for the toxic pollutants cadmium, selenium, and zinc.

SECTION 11

REFERENCES

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SECTION 12

COBALT SALTS INDUSTRY

INDUSTRIAL PROFILE

General Description

The cobalt salts considered in this subcategory are cobalt chloride, cobalt nitrate, and cobalt sulfate. Each salt has specialized applications, however many uses are common to two or all three salts. All three salts are used as catalysts, soil additives, and in the manufacture of inks. Two of the cobalt salts have found uses in the manufacture of pigments and vitamins and various applications in the ceramics industry. The status of cobalt as a strategic material combined with recent changes in the world market may tend to limit the use of cobalt and its salts in many applications.

Table 12-1 presents the industry profile for cobalt salts.

There are ten facilities which manufacture cobalt salts. Total annual production of cobalt salts is estimated to be in excess of 3,000 metric tons while total daily flow is estimated to be greater than 40 cubic meters per day (10,500 gpd). In general, wastewater flow as a function of unit production is very low.

General Process Description and Raw Materials

Cobalt salts are produced by reacting cobalt metal with either hydrochloric, sulfuric, or nitric acid. The reactions for the formation of the cobalt salts under consideration are:

$$Co + 2HCl = CoCl_2 + H_2$$

$$Co + H_2SO_4 = CoSO_4 + H_2$$

$$Co + 2HNO_3 = Co(NO_3)_2 + H_2$$

(Nitrogen oxides may also be produced by decomposition reactions of the nitric acid.)

The production of a cobalt salt is a batch process consisting of five primary steps. These five steps are digestion, purification, concentration, crystallization, and filtration. Digestion is simply the dissolving of the cobalt in the appropriate acid. Once the cobalt is dissolved a purification step using chemical addition and filtration may be necessary to

TABLE 12-1. SUBCATEGORY PROFILE DATA FOR COBALT SALTS

Number of Plants in Subcategory	10
Total Subcategory Production Rate	>3,000 kkg/yr
Minimum	<4.5 kkg/yr
Maximum	Confidential
Total Subcategory Wastewater Discharge	>40 m^3/day
Minimum	0
Maximum	19 m^3/day
Types of Wastewater Discharge	
Direct	5
Indirect	3
Zero	2

remove impurities found in the raw materials. The solution may then be concentrated by evaporation. The solution is then cooled causing the cobalt salt to precipitate out of solution. The final step is the removal of the precipitated salt from the solution by centrifugation, filtration, or other settling process. The salt is then dried and packaged, while the supernatant (or mother liquor) is returned to the concentration step. Figure 12-1 presents graphically the above described steps.

WATER USE AND WASTEWATER SOURCES

Water Use

Noncontact cooling water is used for cobalt salts production in the reactor (digestor) and crystallizers, and constitutes the major water use. Water is used in direct process contact as a reaction component. A portion of this water goes into the dry product as its water of crystallization and the remainder is evaporated. Small amounts of water are used for maintenance purposes, washdowns, cleanups, etc., and several plants use water in scrubbers for air pollution. Table 12-2 presents a summary of water usage for the one plant which provided reliable information in its Section 308 questionnaire. Data from other plants was combined with wastewater flows from other products or the plant provided inconsistant information. None of the six plants the Agency or its contractors visited was producing cobalt salts when visited so more data could not be obtained. However, based on the site visit observations and the process chemistry, the data from Plant F117 is considered reliable and representative of process water use and wastewater flows for cobalt salts production.

Wastewater Sources

Noncontact Cooling Water

Noncontact cooling water is the main source of wastewater. This stream is usually not contaminated and is not treated before discharge.

Direct Process Contact

All direct process contact water not evaporated during concentration steps is recycled back into the process. In addition, air pollution control water may be recycled into the process. Finally a small amount of sludge is generated as a result of removing process impurities.

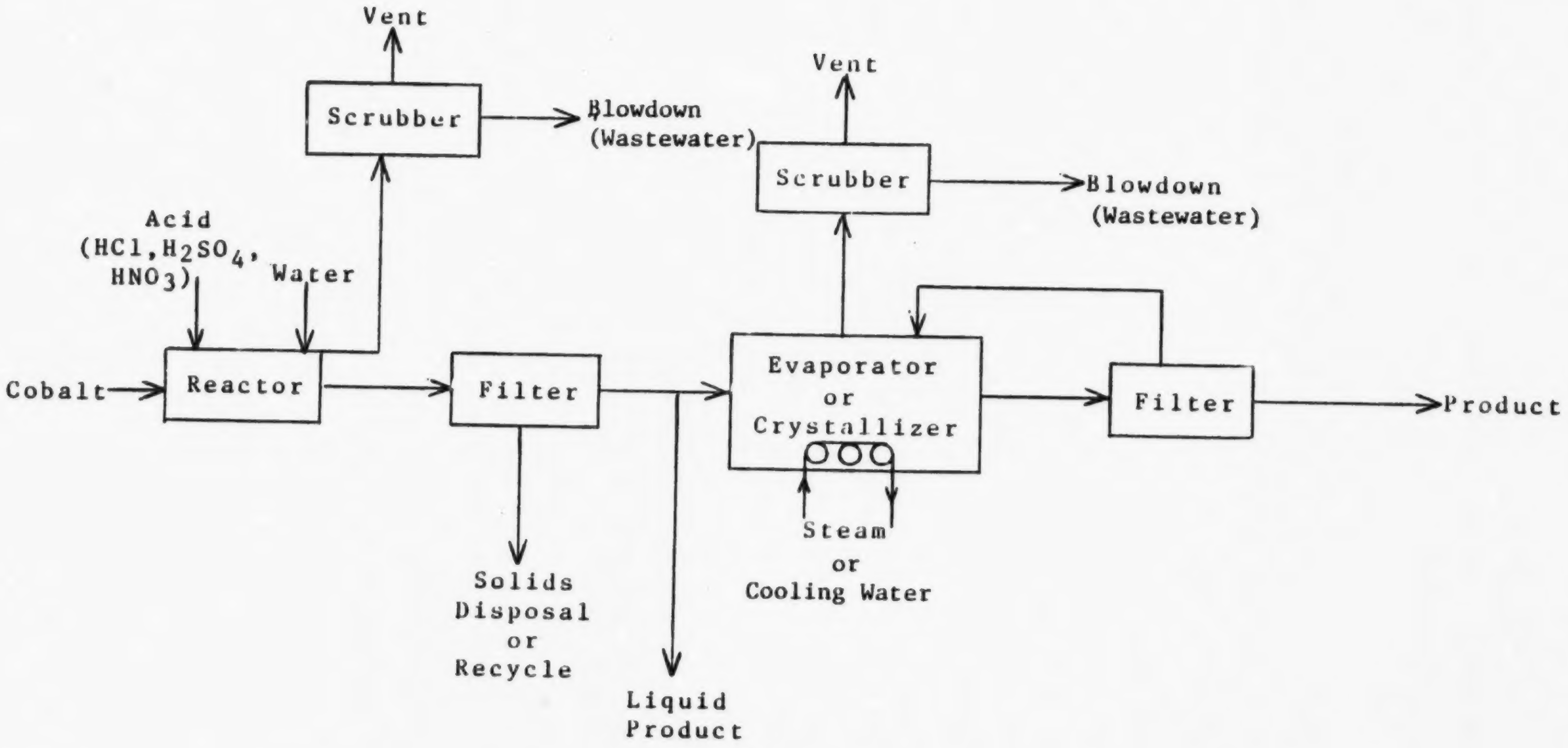
Vent
Scrubber
Blowdown
(Wastewater)
Vent
Scrubber
Blowdown
(Wastewater)
Acid
(HCl, H_2SO_4,
HNO_3)
Water
Cobalt
Reactor
Filter
Evaporator
or
Crystallizer
Filter
Product
Steam
or
Cooling Water
Solids
Disposal
or
Recycle
Liquid
Product

FIGURE 12-1. GENERALIZED PROCESS DIAGRAM FOR COBALT CHLORIDE, SULFATE OR NITRATE.

TABLE 12-2. WATER USAGE AT COBALT SALTS FACILITIES(1)

WATER USE	Flow (m^3/kkg of Cobalt Salts) Plant Designation F117(2)	 F117(3)
Noncontact Cooling	---	---
Direct Process Contact	1.65	1.33
Indirect Process Contact	---	---
Maintenance	NA	NA
Air Pollution Scrubbers	NA	NA
Noncontact Ancillary	---	---
TOTALS	1.65	1.33

NA Flow volume not available.
--- No information.

(1) Values indicated only for those plants that reported separate and complete information.
(2) Cobalt Chloride.
(3) Cobalt Sulfate.

Source: Section 308 Questionnaires and Plant Visit Reports

TABLE 12-3. WASTEWATER FLOW AT COBALT SALTS FACILITIES(1)

	Flow (m^3/kkg of Cobalt Salts)	
	Plant Designation	
WASTEWATER SOURCE	F117(2)	F117(3)
Direct Process Contact	0	0
Indirect Process Contact	0	0
Maintenance	0.083	NA
Air Pollution Scrubbers	0(4)	0(4)
TOTAL PROCESS WASTEWATER DISCHARED	0.083	0
Noncontact Cooling	0	0
Noncontact Ancillary	---	---

NA Flow volume not available.
--- No information.

(1) Values indicated only for those plants that reported separate and complete information.
(2) Cobalt Chloride.
(3) Cobalt Sulfate.
(4) Wastewater recycled within plant.

Source: Section 308 Questionnaires and Plant Visit Reports

Maintenance

Washdowns, cleanups, spills, and pump leaks are periodic and account for the remaining wastewater.

Table 12-3 presents information on sources and quantities of wastewater produced in the production of cobalt salts.

DESCRIPTION OF PLANTS VISITED

Six of the 10 plants producing cobalt salts were visited. Unfortunately, at the time of sampling none of these plants were producing cobalt salts, so that it was not possible to sample wastewater streams associated with cobalt salt production.

The process steps used at each plant are very similar to those described previously.

At Plant F119 cobalt chloride, cobalt nitrate, and cobalt sulfate are produced in addition to many other inorganic compounds. All process wastewater from production of metal products is pH-adjusted to 8.7 - 9.0 with caustic. The neutralized wastewater is sent to a settling basin. Flocculating agents are then added and flow is directed to a tube settler for additional solids removal. The overflow is discharged to a POTW, and the underflow is sent to a sludge holding tank. The supernatant from the sludge holding tank is recycled to the settling basin and the sludge is filtered in a filter press. The filtrate is sent back for more treatment and the filter cake is disposed of in a chemical landfill.

Plant F113 produces cobalt chloride and cobalt sulfate. All process wastewater is discharged to a POTW without treatment except neutralization.

Plant F117 produces cobalt chloride, cobalt nitrate and cobalt sulfate. Separate treatment systems are provided for both the cobalt chloride and cobalt nitrate processes. Each treatment system consists of caustic addition (to pH 10) and filtration before discharge to a surface water. The cobalt sulfate process generates no wastewater.

Plant F107 produces cobalt nitrate as well as other metal salts. All process wastewater is discharged to a POTW without treatment.

Plant F118 produces cobalt nitrate along with other products. The plant has a combined wastewater treatment system with wastewater from all production processes going to the treatment system. The treatment system consists of equalization, chemical addition, precipitation, sedimentation, and final pH adjustment before discharge to surface waters.

Plant F145 produces cobalt chloride and cobalt nitrate in minor quantities in addition to many other chemicals. Wastewater from all production processes, both organic and inorganic are treated in the plant treatment system. Treatment processes used are lime precipitation, clarification, sludge dewatering and biological treatment.

POLLUTION ABATEMENT OPTIONS

Toxic Pollutants of Concern

The toxic pollutants present in cobalt salt process wastewaters depend upon the purity of the sources and the nature of the raw materials being used. Toxic metals which are known to be present in the raw materials are copper, lead, nickel, and zinc. Most of the impurities will be removed in the purification step and disposed of as a solid sludge. There are no raw wastewater data because cobalt salts were not being produced during sampling at the plants visited. However, data submitted by one facility indicated that 4,000 mg/l of cobalt might be expected in a raw wastewater stream. Nickel and copper are also expected to be present in wastewater streams at treatable levels because those metals are present in the cobalt raw material.

Existing Control and Treatment Practices

Wastewater treatment practices for plants visited were previously described above. Provided below are the treatment practices at the four plants not visited.

Plant F124 produces cobalt sulfate and cobalt nitrate as well as other metal salts. Treatment of wastewaters for the entire plant consists of alkaline precipitation, clarification, filter press filtration, multi-media filtration, pH adjustment and sedimentation in ponds before discharging directly to surface waters.

Plant F139 produces cobalt sulfate and cobalt chloride as well as other metal salts. Treatment of wastewaters for the entire plant consists of equalization, sedimentation, filtration, and neutralization before discharge to surface waters.

Plants F150 and F138 have no discharge, as all process wastewater is disposed of by a waste contractor.

Other Applicable Control/Treatment Technologies

Neutralization, clarification, and filtration are practiced for the treatment of cobalt salt process wastewaters at most plants. No demonstrated advanced level technology was identified for this industry.

Process Modifications and Technology Transfer Options

In general, little process wastewater is generated in this subcategory. Most plants minimize the volume of process wastewater generated by:

1. Recycling all direct process contact water back into the process; and
2. Minimizing product changes by careful product scheduling and by increasing the number of reactors.

Caustic soda (rather than lime) may be advantageous when used as an alkaline reagent in wastewater treatment for the following reasons:

1. Caustic soda reduces or eliminates the problem of scale formation;
2. Caustic soda exhibits a faster reaction time and results in better pH control;
3. Caustic soda treatment results in a significant reduction in sludge volume; and
4. The sludge contains high concentrations of the precipitated metal, which may be reclaimed and recycled.

Best Management Practices

The best technology available for the treatment of air pollution scrubber wastewater from cobalt salts production is total recycle. To implement this technology, recycle piping and pumping are needed. At one plant, this technology is being implemented for three cobalt salt products and most plants either recycle the scrubber water or use it as make up water in the reactors.

If contact is possible with leakage, spillage of raw materials or product, all storm water and plant site runoff should be collected and directed to the plant wastewater treatment facility. This contamination can be minimized by indoor storage of chemicals, and proper air pollution control.

If solids from the wastewater treatment plant are disposed or stored on-site, provision must be made to control leachates and permeates. Leachates and permeates which contain toxic pollutants should be directed to the wastewater treatment system for further treatment.

Advanced Treatment Technology

No demonstrated advanced treatment technology has been identified for this subcategory.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1

Level 1 treatment consists of alkaline precipitation, clarification or settling, dewatering of the sludge in a filter press followed by pH adjustment if necessary. This technology is illustrated by Figure 10-10. A holding basin sized to retain 4-6 hours of flow is provided.

The initial treatment step is the addition of caustic soda. This is followed by clarification/settling (if the wastewater characteristics are suitable, a tube settler may be substituted for a clarifier to save space). Sludge is removed from the clarifier and directed to a filter press for dewatering. Pits are provided at the filter press for the temporary storage of sludge. The sludge is periodically transported to a hazardous material landfill. The pH of the treated wastewater stream is adjusted to an acceptable level by acid addition prior to discharge if necessary. A monitoring system is installed at the discharge point. The objective of Level 1 technology is to remove heavy metals and suspended solids.

B. Level 2

Level 2 treatment consists of the addition of granular media filtration following clarification in the Level 1 treatment system. This technology is illustrated in Figure 10-11. Level 2 technology has been selected as a means of achieving improved removal of metal hydroxide precipitates and other suspended solids.

Level 2 treatment was selected as the basis for BPT because it represents a typical and viable industry practice for the control of suspended solids, cobalt, nickel and copper. Currently four of five direct discharge plants in this subcategory have Level 2 or equivalent treatment technology. Two additional plants have no discharge from this process and thus would not incur additional costs.

Equipment for Different Treatment Levels

A. Equipment Functions

Conventional sludge dewatering by a filter press is used for sludge removed by the clarification/settling system. The sludge from the filter press is disposed of off-site in a hazardous material landfill. If a tube settler is used, backwash from the settler is returned to the influent holding basin. Likewise, if granular media filters are used, backwash water is returned to the influent holding basin. After mixing in a tank, the wastewater is filtered prior to pH adjustment (if necessary) and discharged. All equipment is conventional and readily available.

B. Chemical Handling

Caustic soda (50 percent NaOH) is used to precipitate heavy metals in Level 1. Sulfuric acid (concentrated) may be used to reduce the pH of the wastewater prior to discharge.

C. Solids Handling

Treatment sludges generated by Level 1 are dewatered in a filter press. The solids may be disposed of off-site in a hazardous material landfill or sent to an off-site cobalt reclaiming/recovery operation. Level 2 filter backwash may be sent to the head of the plant or, if the solids concentration is sufficiently high, may be sent directly to the filter press.

Treatment Cost Estimates

General

Production ranges and wastewater flow characteristics have been presented earlier in this section and are summarized in Table 12-2. There are five direct dischargers, three indirect dischargers, and two plants which have no discharge.

The average production rate for the five plants providing separate and complete production data is 358 metric tons per year with an average of 115 operating days per year. Only one plant provided relieable flow data but that flow data is believed representative of cobalt salts production based on process chemistry and engineering visits to six plants by the Agency and

TABLE 12-4. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Cobalt Salts

ANNUAL PRODUCTION: 358 METRIC TONS

DAILY FLOW: 0.26 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2	3	4	5
Facilities					
Installed Equipment (Including Instrumentation)	6.6	0.4			
Engineering	1.3	0.1			
Contractor Overhead and Profit	1.2	0.1			
Contingency	0.9	0.1			
Land					
Total Invested Capital	10.0	0.7			
Annual Capital Recovery	1.6	0.1			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	6.0	0.2			
Residual Waste Disposal	1.0	Negl.			
Total Annual Cost	8.6	0.3			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, pH adjustment

LEVEL 2: Filtration

its contractors. Therefore, the model plant for the cobalt salts subcategory has a production rate of 358 metric tons per year and a daily flow of 0.26 cubic meters ($0.083 m^3/kkg$ with 115 operating days assumed). These figures were used as the basis for treatment cost estimates for both levels.

Material usage for both levels was estimated as follows:

Chemical	Amount	Treatment Level
NaOH (50 percent sol.)	3.3 kg/day	1
H_2SO_4 (100 percent)	0.05 kg/day	1

Total solid waste generated is estimated below (Level 2 is incremental to level 1):

Level	Solid Waste
1	$0.024\ m^3$/day
2	$0.00004\ m_3$/day

Model Plant Treatment Costs. Based on of the model plant specifications and design concepts presented earlier and in Section 10, the estimated costs of treatment for one model with two levels are shown in Table 12-4. The cost of level 2 is incremental to Level 1.

Basis for Regulations

Basis for BPT Limitations

A. Technology Basis

For BPT, the Agency is setting limitations based upon alkaline precipitation, clarification, granular media filtration, dewatering of the sludge in a filter press followed by pH adjustment (if necessary). Of the five direct dischargers in this subcategory, four of five have this technology or its equivalent installed. Two additional plants have no discharge and thus would not be affected.

B. Flow Basis

As described above under model plant treatment costs, for the cobalt salts subcategory $0.083\ m^3/kkg$ was selected as being representative of the group.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are being established is based on an evaluation of the wastewater data from discharge monitoring reports, consideration of the raw materials used in the process, literature data, permit applications, and the treatability of the toxic pollutants.

Tables 8-1 through 8-14 summarize the achievable concentrations of toxic metal pollutants from the literature using available technology options, other industries, and treatability studies. Water use and discharge data are presented earlier in Section 12 together with generalized process characteristics. Data from Appendix A on the performance of in-place industry treatment systems were also utilized in developing the list of pollutants to be regulated.

Copper and nickel are commonly found as secondary constituents of many cobalt ores, therefore the two toxic metals would be expected to occur in raw materials used in production of cobalt salts. The copper and nickel impurities would be carried over in the process wastewater, and therefore these two metals were selected as candidate toxic metals for BPT regulations. The non-conventional pollutant, cobalt, was also selected for limitation. Lead and zinc were not selected for limitation because, as described in Sections 7 and 8, control of copper and nickel will provide adequate control of lead and zinc.

Consideration of industry data and information in Section 8 related to the effectiveness of hydroxide precipitation, clarification and filtration lead to the selection of cobalt, copper and nickel as pollutants to be regulated.

D. Basis of BPT Pollutant Limitations

Limitations are presented as both concentrations (mg/l) and loads (kg/kkg), and the relationship between the two is based on the unit flow rate of $0.083m^3/kkg$.

BPT limitations, which apply to all process wastewater discharged, are presented in Table 12-5.

1. Conventional Pollutants

a. pH

The treated effluent is to be controlled within the range of 6.0 - 9.0. This limitation is based upon the data presented in Appendix B of the Development Document for Proposed Effluent

Guidelines for Phase I Inorganic Chemicals (Ref. 1) and the JRB study (Ref. 2).

b. TSS

The BPT limitations for TSS are based upon an average of long-term data from Plants A and K (Phase I Development Document). Both plants are using dual-media filtration to reduce TSS and toxic metals which is the technology basis for the promulgated BPT for the cobalt salts subcategory. Removal of suspended solids by a dual-media filter is a mechanical process independent of the type of solid. Therefore, the TSS effluent quality should be the same for cobalt salts plants as for plants A and K. No long-term TSS data from cobalt salts plants using dual-media filtration is available. A long-term average of 9.3 mg/l (the average of both plants) was used to develop the discharge limitations for plants employing filtration. Variability factors, also obtained from Plants A and K, of 1.8 for a monthly average and 3.0 for a 24 hour maximum were used yielding TSS concentration limits of 17 mg/l and 28 mg/l, respectively. Thus utilizing these values, one obtains TSS mass limitations for the cobalt salts subcategory of:

30-day average:

$(17\ \mathrm{mg/l})(0.083\mathrm{m^3/kkg})(\mathrm{kg}/10^6\ \mathrm{mg})(1000\ \mathrm{l/m^3})$
$= 0.0014\ \mathrm{kg/kkg}$

24-hour maximum

$(28\ \mathrm{mg/l})(0.083\mathrm{m^3/kkg})(\mathrm{kg}/10^6\ \mathrm{mg})(1000\ \mathrm{l/m^3})$
$= 0.0023\ \mathrm{kg/kkg}$

2. Non-Conventional Pollutants

a. Cobalt

The BPT Limitations for cobalt are based on long-term monitoring data from Plant 124 presented in Appendix A. The plant is achieving a long-term average concentration of 0.97 mg/l. Variability factors of 1.44 for a 30-day average and 3.75 for a 24-hour maximum were used yielding cobalt limitations of 1.4 and 3.6 mg/l respectively.

Thus, utilizing these values, mass limitations may be obtained as follows:

30-day average:

$(1.4\ mg/l)(0.083m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.00012\ kg/kkg$

24-hour maximum:

$(3.6\ mg/l)(0.083m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.00030\ kg/kkg$

3. Toxic Pollutants

a. Copper

Since there is no long-term monitoring data for copper from any cobalt salts manufacturing plants, the BPT limitations for copper are based on the long-term monitoring data for nickel at Plant F124. Plant F124 manufactures cobalt salts and nickel salts. The BAT effluent limitations for the nickel sulfate subcategory, which were supported by our treatability study for the nickel sulfate subcategory (see Section 14) show that the copper and nickel concentrations in effluent from the Level 2 treatment system are the same in nickel sulfate wastewater. Since the treatment system is the same for cobalt salts and nickel salts, and at least half the existing dischargers in the cobalt salts subcategory also manufacture nickel sulfate or other nickel salts and commingle the wastewater for treatment, it is reasonable to assume that the copper concentration in treated cobalt salts wastewater is the same as the nickel concentration in that wastewater. The long-term average nickel concentration in treated wastewater at Plant F124 is 0.69 mg/l, with variability factors of 1.52 for a 30-day average and 4.83 for a 24-hour maximum. Using these figures, the corresponding copper concentrations are 1.0 and 3.3 mg/l respectively. Utilizing these figures, mass limitations for copper are calculated as follows:

30-day average:

$(1.0\ mg/l)(0.083m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$

TABLE 12-5. BPT EFFLUENT LIMITATIONS FOR COBALT SALTS

			Conc. Basis (mg/l)		Effluent Limit (kg/kkg)	
Conventional Pollutants	Long-Term Avg. (mg/l)	VFR	30-day avg.	24-hr. max.	30-day avg.	24-hr. max.
TSS(3)	9.3(1)	1.8/3.0(1)	17	28	0.0014	0.0023
Non-Conventional Pollutants						
Cobalt(4)	0.97(2)	1.44/3.75(2)	1.4	3.6	0.00012	0.0003
Toxic Pollutants						
Copper(4)	0.69(2)	1.52/4.83(2)	1.0	3.3	0.000083	0.00027
Nickel(4)	0.69(2)	1.52/4.83(2)	1.0	3.3	0.000083	0.00027

LTA = Long-term average achievable level.

VFR - Variability Factor Ratio (30-day avg./24-hr. max.)

(1) Based upon long-term data at Plants A and K (Phase I).
(2) Based upon long-term data at Plant F124.
(3) Also applicable to NSPS and BCT.
(4) Also applicable to BAT and NSPS.

= 0.000083 kg/kkg

24-hour maximum:

(3.3 mg/l)(0.083 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.00027 kg/kkg

b. Nickel

The BPT limitations for nickel are based upon a long-term average of 0.69 mg/l obtained from 26 months of monitoring at Plant F124 (657 data points). No other long-term monitoring data is available from any cobalt salts manufacturing plant with a Level 2 treatment system. Variability factors of 1.52 for a 30-day average and 4.83 for a 24-hour maximum were used yielding nickel limitations of 1.0 and 3.3 mg/l respectively. Utilizing these values, mass limitations for nickel may be obtained as follows:

30-day average:

(1.0 mg/l)(0.083 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.000083 kg/kkg

24-hour maximum:

(3.3 mg/l)(0.083 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
(= 0.00027 kg/kkg

Basis for BCT Effluent Limitations

On October 29, 1982, EPA proposed a revised BCT methodology. While EPA is considering revising that proposed methdology, in this subcategory no additional technologies were identified which would remove significant additional quantities of conventional pollutants. Accordingly, EPA has determined that BCT equals BPT in this subcategory. As a result, BCT for TSS is equal to the BPT limitations.

Basis for BAT Effluent Limitations

Application of Advanced Level Treatment

For BAT, the Agency is promulgating limitations based on treatment consisting of Level 1 plus Level 2 (BPT) technology because we identified no other technology which would remove significant additional amounts of pollutants. Pollutants limited by the BAT regulation are cobalt, copper and nickel at the same concentration levels and loadings proposed for BPT.

A. Technology Basis

Alkaline precipitation, clarification, filtration, dewatering of the sludge in a filter press, followed by pH adjustment if necessary, is used for BAT which is the same technology used for BPT.

B. Flow Basis

A unit wastewater flow rate of $0.083 m^3/kkg$ of cobalt salts has been selected for BAT (same as BPT).

C. Selection of Pollutants to be Regulated

Toxic Pollutants

The non-conventional pollutant cobalt, and toxic polutants copper and nickel have been selected at the same concentration levels and loadings promulgated for BPT. Table 12-5 presents the BAT limitations for Cobalt Salts Subcategory (BAT=BPT).

Basis for NSPS Effluent Limitations

For NSPS, the Agency is promulgating limitations equal to BAT since no additional technology which would remove significant additional amounts of pollutants has been identified. The pollutants limited are pH, TSS, cobalt, copper, and nickel. The limitations are presented in Table 12-5.

Basis for Pretreatment Standards

The Agency is promulgating PSES and PSNS that are equal to BAT limitations because BAT provides better removal of cobalt, copper, and nickel than is achieved by a well-operated POTW with secondary treatment and, therefore, these toxic pollutants would pass through a POTW in the absence of pretreatment. Pollutants regulated under PSES and PSNS are cobalt, copper, and nickel.

The Agency has no screening and verification data to use to estimate the raw waste concentrations for the cobalt salts subcategory. One company reported one sample of a cobalt salt raw wastewater contained 4000 mg/l of cobalt but did not have any data on any toxic metals in the cobalt salt wastewater. The cobalt salts are produced from cobalt metal. Commerical grade cobalt is, on average 99.5% pure, with the range from 99 to 99.9% pure cobalt. The major impurities are copper and nickel, with smaller amounts of silicon, manganese, iron, carbon, lead, and zinc. The amount of each depends upon the source of the ore from which the cobalt was refined. Since the source of the cobalt cannot be predicted for any cobalt salt manufacturing plant, and may vary at any plant from time to time, the Agency has assumed that the copper and nickel are equally probable and together account for about half the impurity in average commerical grade cobalt. That is, for 99.5% pure cobalt, 0.25% is copper and nickel, and the copper is assumed to be 0.125% and the nickel is 0.125% of the total metal. The primary source of the process wastewater at cobalt salts manufacturing plants is spillage. We assume that the spill contains cobalt and other impurities in the same ratio as found in the purchased cobalt, i.e., copper and nickel are each about 0.125% of the concentration of the cobalt in the wastewater. Therefore, for a cobalt concentration of 4000 mg/l, the copper concentration would be 4000 x .00125 = 5 mg/l, and the nickel concentration would also be 5 mg/l.

In the absence of any other raw waste data for cobalt salts manufacturing the Agency has used these calculations to estimate the percent removals for cobalt, copper, and nickel by applying the selected BAT technology to the untreated wastewater. The calculations for percent removals are as follows:

Cobalt: Raw waste = 4000 mg/l
BAT = 0.97 mg/l

Percent Removal = [(4000 -0.97)] ÷ (4000)] (100)
= 99.98%

Copper: Raw waste = 5 mg/l
BAT = 0.69 mg/l

Percent Removal = [(5 - 0.69) ÷ (5)] (100)
= 86.2%

Nickel: Raw waste = 5 mg/l
BAT = 0.69 mg/l

Percent Removal = [(5 - 0.69) ÷ (5)] (100)
= 86.2%

These estimated removals are greater than the removals achieved for copper (58%) and nickel (19%) by 25% of the POTWs in the "50 Cities" study (Fate of Priority Pollutants in Publicly Owned Treatment Works, Final Report, EPA 440/1-82/303, September, 1982). Limited information showing the removal of cobalt is available but the removals by 25% of the POTWs in that study for other toxic metals range from 19% tc 66%. Presumably, the removals for cobalt would be in that range because cobalt behaves similarly to other toxic metals. Therefore, since BAT technology achieves a greater percent removal of cobalt, copper, and nickel than is achieved by a well operated POTW with secondary treatment, those three metals would pass through a POTW in the absence of pretreatment.

Existing Sources

There are currently three indirect discharging cobalt salts plants in the subcategory. For Pretreatment Standards for Existing Sources (PSES), the Agency is promulgating limitations based on BAT described above. The pollutants limited are cobalt, copper, and nickel as presented in Table 12-5.

New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is setting limitations based on NSPS. Since NSPS is equal to BAT, Table 12-5 summarizes the limitations for the nonconventional pollutant cobalt and toxic pollutants copper and nickel.

SECTION 12

REFERENCES

1. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category," EPA Report No. 440/1-79-007, June 1980.

2. JRB Associates, Inc., "An Assessment of pH Control of Process Waters in Selected Plants," Draft Report to the Office of Water Programs, U.S. Environmental Protection Agency, 1979.

SECTION 13

COPPER SALTS INDUSTRY

INDUSTRIAL PROFILE

General Description

The copper salts included in this subcategory are copper sulfate, copper chloride, copper carbonate, copper nitrate, and copper iodide. These compounds are produced by several different processes.

A process description and discussion of the copper sulfate industry can be found in the Phase I development document:

> Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-82-007, June 1982.

Briefly, copper sulfate is produced by reaction of copper, copper oxide, or waste copper (such as spent plating bath) with sulfuric acid:

$$Cu + H_2SO_4 = CuSO_4 + H_2$$

The copper sulfate may be sold in solution as produced, or may be purified and crystallized before sale as the solid. Detailed process information and the results of screening and verification sampling are provided in the Phase I development document. Therefore, the following discussion will cover the other copper salts included in this subcategory.

Most copper chloride is marketed as cuprous chloride ($CuCl$). It is used as a catalyst, decolorizer, and desulfurizing agent in the petroleum industry, in the denitration of cellulose, and for many other applications. The other form of copper chloride is cupric chloride, produced as an intermediate in some cuprous chloride processes. Cupric chloride ($CuCl_2$) has many applications such as a catalyst in a number of organic oxidation reactions, in sweetening petroleum oils, a wood preservative, and in other uses. Both cuprous and cupric chloride can be produced as either a liquid solution or as dried crystals.

Copper carbonate ($CuCO_3$) is produced as a dry product and is normally produced for outside sale. It is used in pyrotechnics, paint and varnish pigments, ceramic frits, in the electroplating

TABLE 13-1. SUBCATEGORY PROFILE DATA FOR COPPER SALTS
(a) COPPER SALTS EXCLUSIVE OF COPPER SULFATE

Number of Plants in Subcategory	15
Total Subcategory Production Rate	>3000 kkg/yr
Minimum	<4.5 kkg/yr
Maximum	640 kkg/yr
Total Subcategory Wastewater Discharge	~2000 m^3/day
Minimum	0
Maximum	1060 m^3/day
Types of Wastewater Discharge	
Direct	4
Indirect	5
Zero	6

TABLE 13-1. SUBCATEGORY PROFILE DATA SUMMARY FOR COPPER SALTS

(b) COPPER SULFATE(1)

Total Subcategory Capacity Rate	Indeterminate
Total Subcategory Production Rate	27,300 kkg/year
Number of Plants in this Subcategory	16
308 Data on File for	10
With total capacity of	38,850 kkg/year
With total production of	21,420 kkg/year
Representing capacity	
Representing production	78 percent
Plant production range:	
Minimum	45 kkg/year
Maximum	9,100 kkg/year
Average production	2,100 kkg/year
Median production	790 kkg/year
Average capacity utilization	63 percent
Plant age range:	
Minimum	3 years
Maximum	52 years
Waste water flow range:	
Minimum	0 cubic meters/day
Maximum	45 cubic meters/day
Volume per unit product:	
Minimum	0 cubic meter/kkg
Maximum	23 cubic meter/kkg

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(1) Source: page 632 of Draft development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-82/007; June,1982.

Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977, U.S. Department of Commerce, Current Industrial Reports, December, 1977; Energy and Environmental Analysis, Inc.; Draft Report, "Preliminary Economic Assessment of Effluent Limitations in the Inorganic Chemical Industry," June, 1978 and "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

industry as a source of copper, and agriculturally as a fungicide for treating seed.

Copper nitrate ($Cu(NO_2)_3$) can be sold in crystal or solution form. It is used in light-sensitive reproductive papers, as a ceramic color, as a mordant and oxidant in textile dyeing and printing, in nickel-plating baths and aluminum brighteners, and as a catalyst for numerous organic reactions.

Copper iodide (CuI) is produced and sold in a powder form. It is used as a catalyst in certain organic reactions, as an ice-nucleating chemical, and as a coating in cathode ray tubes. Table 13-1 is a profile data summary for the copper salts subcategory.

There are 15 facilities producing copper salts. Six facilities have no discharge, four discharge directly and five discharge indirectly. Of the 15 producers of other copper salts, six are known to produce copper sulfate as well.

Total annual production in this subcategory is estimated to be in excess of 3,000 metric tons, while total daily wastewater flow is estimated to be approximately 2,000 cubic meters. It has been found that copper carbonate production accounts for over 90 percent of the wastewater flow in this subcategory.

General Process Description and Raw Materials

The four copper salts exclusive of copper sulfate are produced by different processes, each discussed separately below.

Copper chloride is produced in two forms, cupric chloride ($CuCl_2$) and cuprous chloride ($CuCl$). Each product involves the reaction of copper with chlorine, and may be produced in solid or solution form. The general reactions are:

$$Cu + 1/2\ Cl_2 = CuCl$$

$$Cu + Cl_2 = CuCl_2$$

$$CuCl_2 + 3Cu + Cl_2 = 4\ CuCl$$

Copper chloride (cuprous or cupric) is manufactured in a solid form by reacting chlorine and pure copper in a molten bath. The molten copper chloride is withdrawn continuously and materials are added to maintain the desired material balance. The molten copper chloride is cast, cooled, and if desired, ground to a powder.

COPPER CHLORIDE

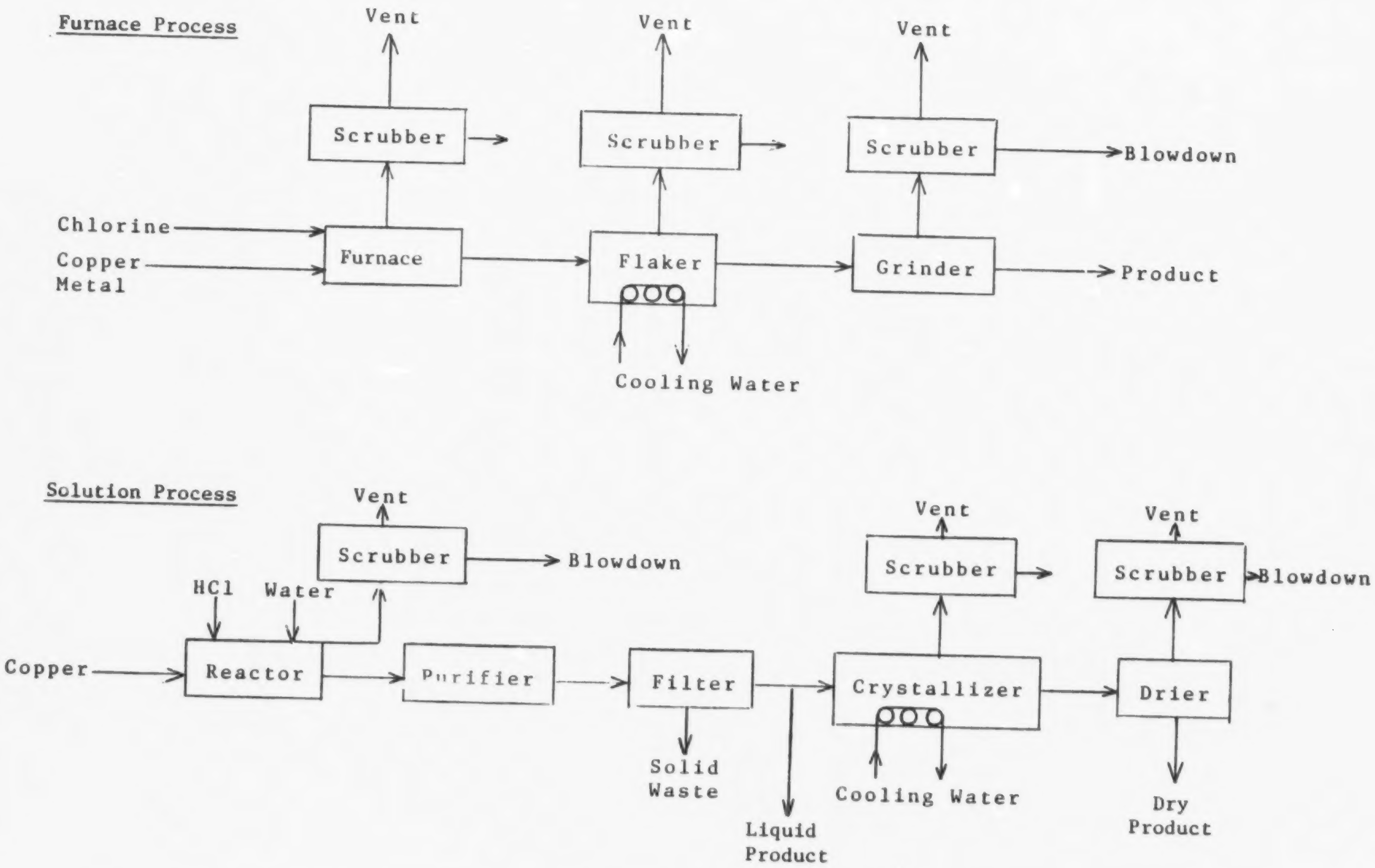

Furnace Process
Vent
Vent
Vent
Scrubber
Scrubber
Scrubber
Blowdown
Chlorine
Copper Metal
Furnace
Flaker
Grinder
Product
Cooling Water
Solution Process
Vent
Scrubber
Blowdown
HCl
Water
Copper
Reactor
Purifier
Filter
Solid Waste
Liquid Product
Vent
Scrubber
Crystallizer
Cooling Water
Vent
Scrubber
Blowdown
Drier
Dry Product

FIGURE 13-1. GENERALIZED PROCESS FLOW DIAGRAM FOR COPPER CHLORIDE.

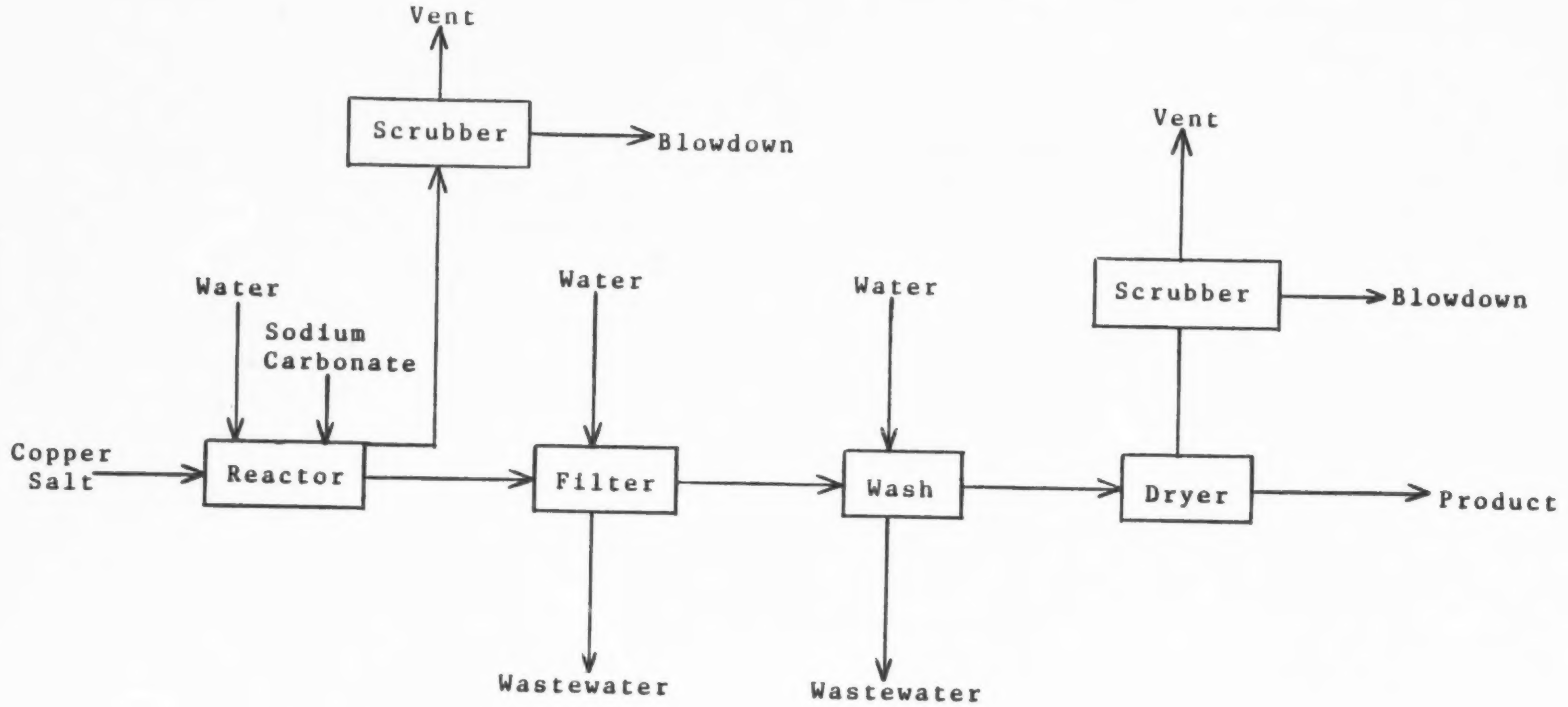

Vent
Scrubber
Blowdown
Vent
Water
Sodium Carbonate
Water
Water
Scrubber
Blowdown
Copper Salt
Reactor
Filter
Wash
Dryer
Product
Wastewater
Wastewater

FIGURE 13-2. GENERALIZED PROCESS FLOW DIAGRAM FOR COPPER CARBONATE.

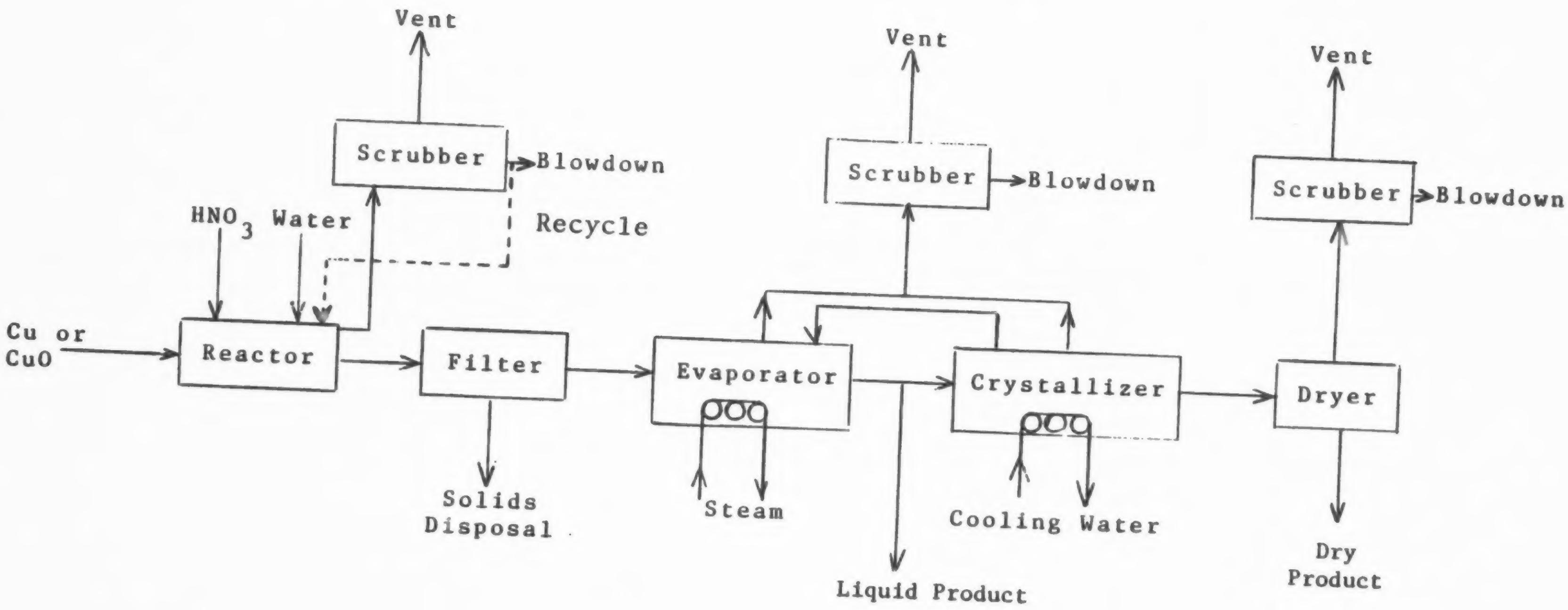
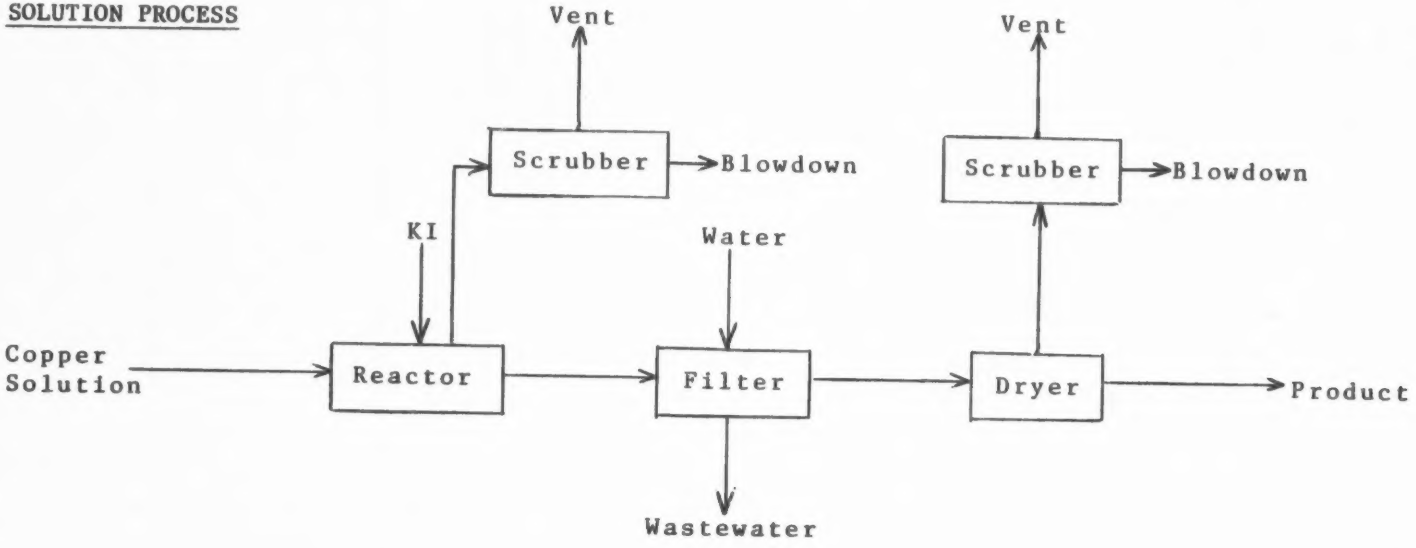

Vent
Scrubber
Blowdown
Recycle
HNO_3
Water
Cu or CuO
Reactor
Filter
Solids Disposal
Vent
Scrubber
Blowdown
Evaporator
Steam
Liquid Product
Crystallizer
Cooling Water
Vent
Scrubber
Blowdown
Dryer
Dry Product

FIGURE 13-3. GENERALIZED PROCESS FLOW DIAGRAM FOR COPPER NITRATE.

SOLUTION PROCESS


Vent
Vent
Scrubber
Blowdown
Scrubber
Blowdown
KI
Water
Copper
Solution
Reactor
Filter
Dryer
Product
Wastewater

FURNACE PROCESS

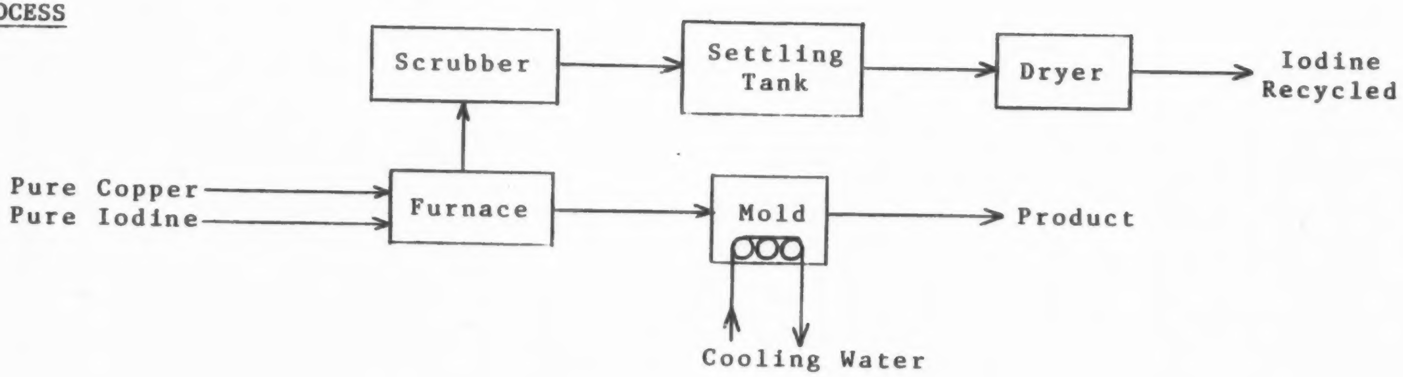

Scrubber
Settling
Tank
Dryer
Iodine
Recycled
Pure Copper
Pure Iodine
Furnace
Mold
Product
Cooling Water

FIGURE 13-4. GENERALIZED PROCESS FLOW DIAGRAMS FOR COPPER IODIDE.

Copper chloride in solution form is manufactured by reacting copper, chlorine and hydrochloric acid which acts as a solvent in the reaction. The cuprous form also requires cupric chloride as a starting material. The resulting solution may be purified, filtered and then crystallized. Various forms of copper feed material may be used, such as pure copper, copper oxide and spent plating and etching solutions. Figure 13-1 presents the general process diagram for these processes.

Copper carbonate is produced by reacting either copper sulfate or copper nitrate with sodium carbonate in water to precipitate copper carbonate. The general reactions are:

$$CuSO_4 + Na_2CO_3 = CuCO_3 + Na_2SO_4$$

$$Cu(NO_3)_2 + Na_2CO_3 = CuCO_3 + 2NaNO_3$$

The product is decanted to remove the sodium sulfate or sodium nitrate solution and washed to remove impurities. The pure copper carbonate product is then milled, dried and packaged. Figure 13-2 presents the general process diagram for the production of copper carbonate.

Copper nitrate is produced by the reaction of pure copper or copper oxide with nitric acid. The general reactions for pure copper are:

$$3Cu + 8\ HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$$

The resulting solution is treated and filtered to remove impurities. The residue from filtration is disposed of as a solid waste. The filtrate is treated in a boil tank to drive off water forming a saturated copper nitrate solution which is then cooled in a crystallizer to crystallize the product. The liquid from crystallization is generally recycled. The slurried product is recovered, dried and packaged. Figure 13-3 presents the general diagram for the production of copper nitrate.

Copper iodide (CuI) is produced by two methods. The general reactions are:

$$CuSO_4 + 2KI = CuI + K_2SO_4 + 0.5I_2$$

$$2Cu + I_2 = 2CuI$$

The first process involves the precipitation of cuprous iodide by reacting a copper salt (i.e., copper sulfate) and potassium iodide. A reducing agent may be used to prevent contamination of the cuprous iodide by reacting with the liberated iodine. The cuprous iodide slurry is collected, washed in a filter press, dried, ground, and packaged. The second process requires finely divided copper metal and elemental iodine. These are mixed and fed into a furnace. Molten cuprous iodide flows from the bottom into a mold which is cooled by water. Iodine vapor is collected by a scrubber, settled and periodically reused. Figure 13-4 presents the general process diagrams for this product.

WATER USE AND WASTEWATER SOURCES

Water Use

The major use of water in the production of copper chloride is noncontact cooling water. Direct contact process water is used in the reaction process for copper chloride solution. In addition, water is also used for air pollution control, maintenance, washdowns, and noncontact ancillary uses.

The major water use in the production of copper carbonate is direct contact process water used to wash the precipitated product. Indirect process water is also used along with noncontact ancillary uses.

Noncontact cooling water used in the crystallizer is the major use of water in the production of copper nitrate in solid form. Water is also used for air pollution control, maintenance, washdowns, and noncontact ancillary uses.

In the production of copper iodide noncontact cooling water is used in the furnace process and direct contact water may be used for product washing in the solution process. Water may also be used in air pollution control devices.

Table 13-2 presents a summary of available plant data on water use.

Wastewater Sources

Noncontact Cooling Water

Noncontact cooling water is used to cool reaction vessels in the production of the copper salts, with the exception of copper carbonate. This wastewater stream should not be contaminated by process leaks, and therefore can be discharged without treatment.

Direct Process Contact Water

TABLE 13-2. WATER USAGE AT COPPER SALTS FACILITIES(1)

Water Use	Flow (m^3/kkg of Copper Salts)									
	Plant Designation									
	F142(2)	F127(2)	F115(2)	F116(3)	F129(3)	F108(4)	F132(4)	F113(4)	F133(5)	F130(4)
Noncontact Cooling	0	0	0	8.44	0	20.5	49.2	7.52	0	NA
Direct Process Contact	21.3	53.8	55.6	0	1.65	0	0	0	2.33	15.9
Indirect Process Contact	Small Amount	Small Amount	60.7	0	1.65	0	0	0.83	NA	NA
Maintenance	Small Amount	Small Amount	NA	NA	NA	NA	NA	NA	0.22	1.51
Air Pollution Scrubbers	0	0	---	0.21	0	0.07	4.12	1.57	16.03	NA
Noncontact Ancillary	0	0	0.14	0	0	0	20.5	0.52	0.51	NA
TOTALS	21.3	53.8	116.4	8.65	3.30	20.57	73.8	10.44	19.09	17.41

NA Flow volume not available.
--- No information.

(1) Values indicated only for those plants that reported separate and complete information.
(2) Copper carbonate.
(3) Copper iodide.
(4) Copper chloride.
(5) Copper nitrate.

Source: Section 308 Questionnaires and Plant Visit Reports

TABLE 13-3. WASTEWATER FLOW AT COPPER SALTS FACILITIES(1)

Wastewater Source	Flow (m^3/kkg of Copper Salts)									
	Plant Designation									
	F142(2)	F115(2)	F127(2)	F116(3)	F129(3)	F108(4)	F113(4)	F130(4)	F132(5)	F133(5)
Direct Process Contact	13.3	55.6	44.8	0	1.65(6)	0	0	0	0	0
Indirect Process Contact	Small Amount	60.8	Small Amount	0	1.65(6)	0	0.83	0	0	0
Maintenance	Small Amount	NA	Small Amount	NA	NA	NA	NA	1.51(6)	NA	0.93
Air Pollution Scrubbers	0	---	0	0	0	0.07(6)	1.57(6)	0	4.12(6)	16.03(6)
TOTAL PROCESS WASTEWATER DISCHARGED	13.3	116.4	44.8	0	0	0	0.83	0	0	0.93
Noncontact Cooling	0	0	0	8.44	0	20.5	7.52	0	49.2	0
Noncontact Ancillary	0	0.14	0	0	0	0	0.52	0	20.5	0.51

NA Flow volume not available.
--- No information.

(1) Values indicated only for those plants that reported separate and complete information.
(2) Copper carbonate.
(3) Copper iodide.
(4) Copper chloride.
(5) Copper nitrate.
(6) Wastewater recycled within plant. (Total recycle.)

Source: Section 308 Questionnaires and Plant Visit Reports

Direct process contact water is used in the production of copper carbonate and may be used in the production of copper iodide. The direct contact water originates from product washings, decants of sodium sulfate and sodium nitrate, and filtration to remove impurities. Solid wastes are disposed of at a landfill while remaining solutions are usually discharged.

Noncontact Ancillary

A few plants that manufacture copper nitrate use steam as the heat source in the evaporators. The steam condensate is noncontact ancillary wastewater. This can be discharged without treatment.

Indirect Process Contact

Washdown, pump seal leaks, and spills are sources of indirect contact wastewater. Depending on the plant and product, these flows may or may not be a major source of wastewater. Wastewater emanating from this source is either recycled or discharged. For most copper salts, including copper sulfate, but not copper carbonate, the major source of process wastewater is washdown, pump seal leaks, and spills.

Air Pollution Control

Wet scrubbers are frequently used to control the discharge of fumes from reaction tanks and evaporators or concentrators. Blowdown from these scrubbers may be intermittent or continuous process wastewater. Scrubber wastewater generated from copper nitrate production is frequently recycled as make-up water into the copper nitrate reactor. All plants providing information on air scrubber wastewater recycle that wastewater either within the scrubber system or as make-up water for the reactors.

Sludge

Solid waste can be generated in product purification by the filtration step in copper salts manufacture. The filtration step is usually only necessary when plants utilize impure copper as a raw material. These filter sludges contain metallic impurities and require disposal at a hazardous waste landfill. No solid waste is generated at plants that produce copper chloride in liquid form. Plants utilizing pure copper feedstock are able to eliminate, reduce or recycle most contact wastes.

The available data concerning wastewater flows at copper salts facilities is summarized in Table 13-3. Facilities F142, F115, and F127 produce copper carbonate, while the remaining facilities listed in the table do not. It is observed that the copper carbonate facilities produce substantially more process wastewater than do other copper salts facilities. This difference is attributable to the greater quantities of wash water required for removal of product impurities in the copper carbonate production process. The typical wastewater flow at copper sulfate plants is 0.94 m^3/kkg, and results from indirect contact water use (See the Phase I Development Document, page 649).

DESCRIPTION OF PLANTS VISITED AND SAMPLED

Plants Sampled

Plant F130 produces cuprous chloride by the process shown in Figure 13-5. The plant produces cuprous chloride, cupric chloride and other inorganic compounds. Cupric chloride is used almost entirely as an intermediate for cuprous chloride production. The process used at this plant is similar to that described previously for the production of copper chloride from spent plating and etching solutions. The solutions contain dilute cupric chloride and copper ammonium chloride. This solution is then reacted with hydrochloric acid to form a more concentrated cupric chloride solution. Equal amounts of cupric chloride solution and copper metal are reacted together with water and hydrochloric acid to produce the appropriate cuprous chloride solution.

Wastewater originates from tank and drum washdown, and pump seal leaks. All washes from tank and loading areas are directed to a sump where it is collected and transferred to the wastewater holding tank. All wastewater and sludge collected in the wastewater tank is recycled into the process. Most of the water used in the process is shipped with the product solutions. There is no wastewater treatment facility, consequently no treated wastewater samples could be collected.

During the sampling episode the pump seals were not leaking and water was forced through the seals in order to take a sample. Toxic pollutant concentrations and loads in Table 13-4 were taken from tank and drum washes and not from the collection tank because the tank is only periodically dumped and pollutants have time to settle. Figure 13-5 shows wastewater sources and sampling locations at Plant F130.

Plant F127 produces copper carbonate (Figure 13-6) as well as a variety of other metal products and inorganic chemicals. The process used at this plant is similar to that previously described for the production of copper carbonate. Nearly all

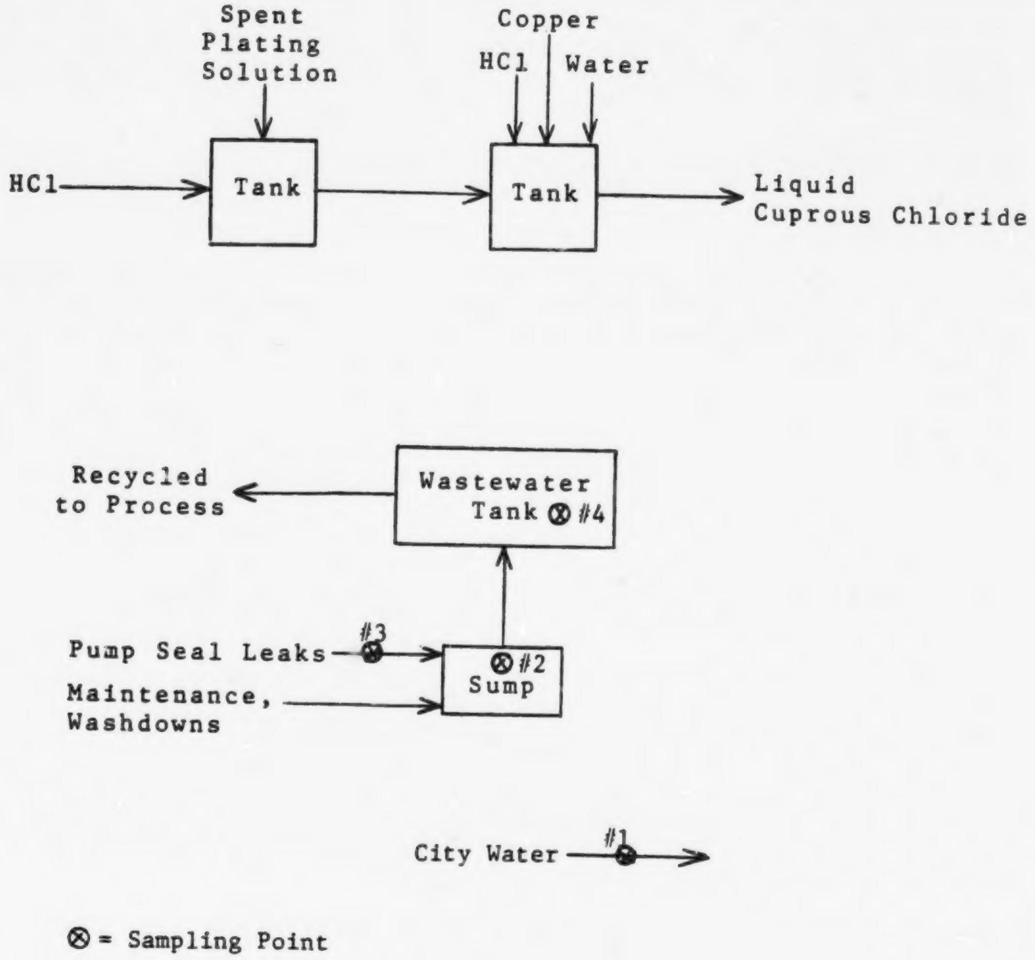

Spent Plating Solution
Copper
HCl
Water
HCl
Tank
Tank
Liquid Cuprous Chloride
Recycled to Process
Wastewater Tank ⊗ #4
#3
Pump Seal Leaks
⊗ #2 Sump
Maintenance, Washdowns
#1
City Water
⊗ = Sampling Point

FIGURE 13-5. PROCESS AND SAMPLING LOCATIONS FOR PLANT F130.

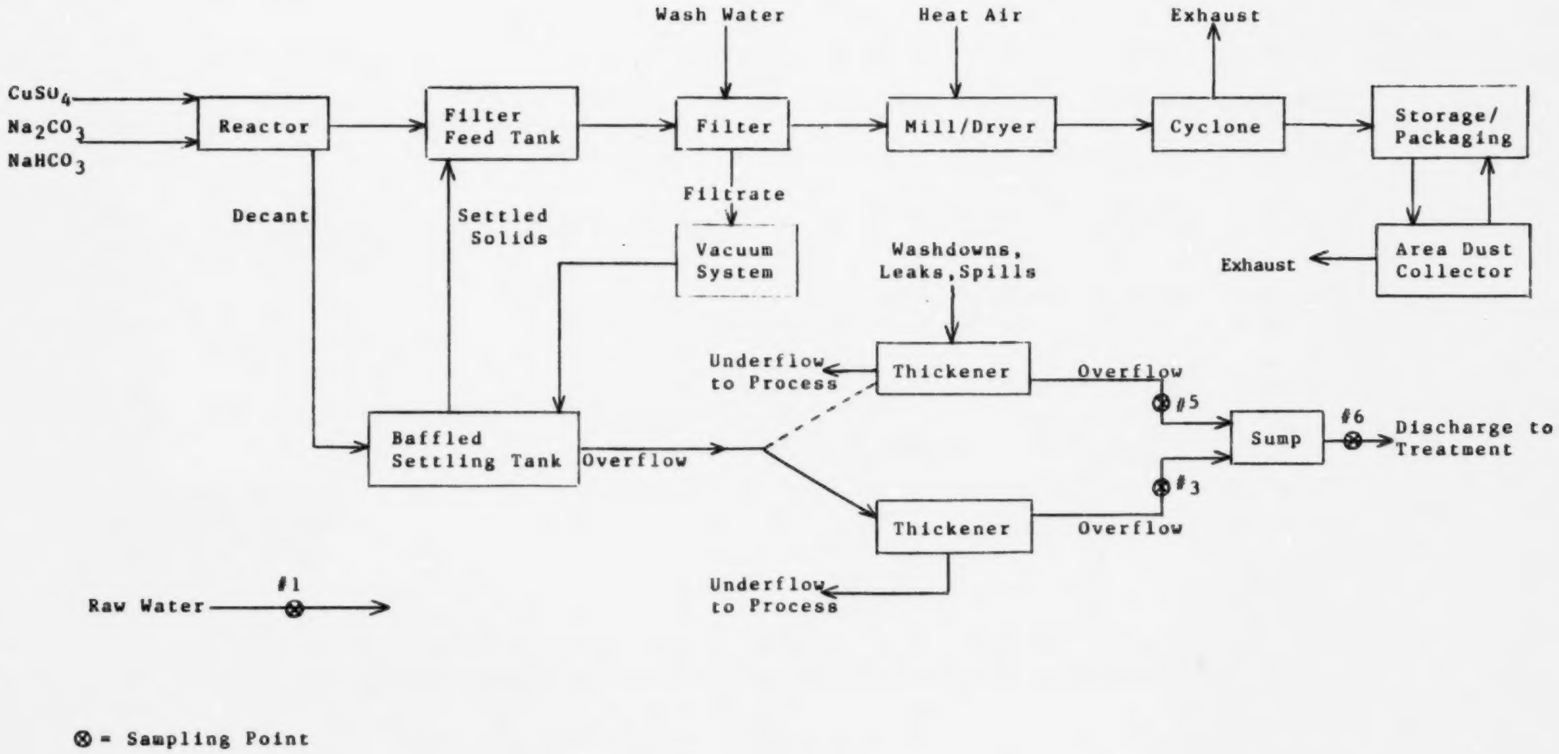

$CuSO_4$
Na_2CO_3
$NaHCO_3$
Reactor
Decant
Filter Feed Tank
Settled Solids
Wash Water
Filter
Filtrate
Vacuum System
Heat Air
Mill/Dryer
Exhaust
Cyclone
Storage/ Packaging
Area Dust Collector
Exhaust
Baffled Settling Tank
Overflow
Washdowns, Leaks, Spills
Underflow to Process
Thickener
Overflow
#5
Sump
#6
Discharge to Treatment
#3
Thickener
Overflow
Underflow to Process
Raw Water
#1
⊗ = Sampling Point

FIGURE 13-6. PROCESS, WASTEWATER FLOW, AND SAMPLING LOCATIONS FOR PLANT F127.

TABLE 13-4. POLLUTANT CONCENTRATIONS AND LOADS FOR SAMPLED COPPER SALTS FACILITIES(1)

		$\frac{mg/l}{kg/kkg}$					
Stream No.	Stream Description	TSS	Cu	Ni	Pb	Sb	Zn
				Plant F127		(Copper Carbonate)	
3.	Raw Process Wastewater	143.5 2.72	129.3 2.45	0.38 0.00720	0.59 0.0112	0.90 0.0170	0.027 0.00051
5.	Raw Floor Washings & Leaks	180.9 6.14	161.7 5.49	0.017 0.00058	0.13 0.00441	0.071 0.00241	0.06 0.00204
6.	Combined Raw Wastewater to Treatment	185.9 9.79	107.0 5.63	0.18 0.00948	0.15 0.00790	0.20 0.0105	0.045 0.00237
				Plant F130		(Cuprous Chloride)	
2.	Tank and Drum Washdown	37.7 0.0367	351.3 0.342	0.36 0.00035	5.72 0.00557	0.483 0.00047	7.07 0.00688
3.	Pump Seals(2)	< 0.5 ---	300.0 ---	0.045 ---	2.90 ---	0.006 ---	0.015 ---
4.	Total Waste Holding Tank(3)	83.7 0.0815	57.8 0.0563	0.261 0.00025	0.308 0.00030	0.703 0.00068	3.12 0.00304

--- Insufficient information.

(1) Average values for three days except where noted.
(2) One-day sampling.
(3) Recycled to process.

water is used as direct contact water in dissolving, reacting, and filter washing. Noncontact cooling water is not used in the process. A majority of the wastewater from the process consists of reaction supernatant decants, filtrate, and filter wash water. These wastewater streams are collected in a settling tank where coarse particulates are settled out and recovered. The overflow is sent to a thickener where additional copper is separated from the wastewater. The settled sludge is recycled back to the process while the thickener overflow is sent to the central treatment system. Floor washings, leaks and spills are directed to another thickener for copper recovery, and the overflow discharged to the central treatment system. At the central treatment system, copper carbonate wastewater is commingled with wastewater from inorganic and organic chemicals manufacture, then subjected to alkaline precipitation, aeration, and clarification before discharge to surface waters. Figure 13-6 shows wastewater sources and sampling locations at Plant F127. Since the central wastewater treatment system treats wastewater from a variety of products, and therefore may not be representative of copper carbonate wastewater only, no sampling was performed at the central treatment system. Table 13-4 presents the wastewater loads and pollutant concentrations for the sampled streams.

Other Plant Visits

Nine plants in the Copper Salts Subcategory were visited but not sampled. A description of the individual products, wastewater treatment, and discharge status for those plants visited are given below.

Plant F145 produces cupric chloride, copper nitrate and other inorganic and organic compounds. The copper chloride process is similar to the process previously described. The resulting solution is purified, filtered to remove impurities, then crystallized. The pure crystals are collected, dried, ground, and sold. The residue from filtration is disposed of as solid waste. Copper nitrate is produced similar to the process previously described. The majority of water used is noncontact cooling water with minimal usage of direct contact water. Scrubber wastes, washings, filtrates, tank cleanouts, and leaks or spills which cannot be recycled are sent to a central treatment system where all plant wastewaters are treated. Treatment consists of equalization, lime precipitation, clarification and sludge dewatering. Overflow from this system is then treated by biological treatment prior to discharge to surface waters.

Plant F119 produces copper nitrate, copper iodide, and copper carbonate. All processes are similar to those previously described. Off- gases from the copper nitrate production are exhausted though a condenser to recover nitric acid, and the off-gases then are incinerated to destroy nitrogen oxides before release to the atmosphere. Dust from the copper iodide and copper carbonate grinding operations are collected in a baghouse, and the recovered dust is disposed of in a chemical landfill. Process wastewaters from all products manufactured are directed to a central treatment system consisting of pH adjustment, settling, flocculation, clarification, and sludge dewatering. The clarifier overflow discharges to a municipal treatment plant while the underflow is dewatered in a filter press before disposal in a chemical landfill.

Plant F118 produces copper carbonate in addition to many other inorganic chemicals. The manufacturing process is similar to the previously described process. Wastewater from all chemical processes are combined and passed through a treatment system consisting of equalization, alkaline precipitation, settling and final pH adjustment before discharge to surface waters.

Plant F113 produces cuprous chloride and other inorganic salts. The manufacturing process is similar to the previously described process for producing molten cuprous chloride from the reaction of copper metal and chlorine. All contact and noncontact wastewater is discharged to a POTW without pretreatment except neutralization.

Plant F142 manufactures copper carbonate. The manufacturing process is similar to the previously described process. Wash waters and filtrates are passed through settling tanks to remove sediments before discharge to a POTW.

Plant F133 manufactures copper nitrate in solution form and other inorganic products. The manufacturing process is similar to the previously described process. The only process wastewater generated is derived from leaks and spills. This small volume of wastewater is sent to a separate copper wastewater treatment unit before being discharged to a central treatment system where all facility wastewater is pretreated prior to discharge to a POTW. The copper treatment system consists of equalization, caustic addition to pH 8-9, sulfide addition, and filter press filtration. The filtrate is then equalized in the central treatment facility, treated with caustic to pH 6-9, and filtered for discharge.

Plant F120 produces copper nitrate and other inorganic products. Wastewater from scrubbers, equipment washdowns, pump seals, maintenance and various other product process are combined, treated with lime and lagooned. The treated wastewater is used to slurry the purification and treatment sludges back to the settling ponds for temporary storage. There was no discharge of process wastewater streams when visited. Since the lagoons are unlined, percolation of some of the wastewater from the lagoons into the subsoil could account for the fact that the plant had no discharge when visited.

Plant F129 produces copper iodide by direct reaction of copper and iodine. This plant has no discharge as all wastewater is recycled since the plant uses pure raw materials only and does not need a purification step. Plants that did not use pure raw materials would need a purification step and thus would have a discharge of process wastewater.

Summary of Toxic Pollutant Data

Thirteen toxic metals and four toxic organics were found at detectable concentrations in the total combined raw wastewater at the two sampled plants. The table below presents the maximum daily concentrations observed for these pollutants found in the total combined raw wastewater. No treated wastewater samples were collected during the sampling program at these facilities, for the reasons given above, pages 263 and 267.

Pollutant	Maximum Concentration Observed (ug/l)
Antimony	1,300
Arsenic	270
Beryllium	3
Cadmium	20
Chromium	270
Copper	560,000
Lead	12,000
Mercury	32
Nickel	390
Selenium	140
Silver	130
Thallium	180
Zinc	8,300
Bis(2-ethylhexyl) phthalate	23
Tetrachloroethylene	30 (28)*
Toluene	27 (29)*
Methyl Chloride	10*

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*preserved samples

TABLE 13-5. TOXIC POLLUTANT RAW WASTEWATER DATA FOR SAMPLED COPPER SALTS FACILITIES

Average Daily Pollutant Concentrations and Loads

$\frac{mg/l}{kg/kkg}$

	Plant Designation		
Pollutant	F130(1)	F127(2)	Overall Average
Antimony	0.483 0.00047	0.200 0.0105	0.341 0.00550
Arsenic	0.100 0.00010	0.103 0.00542	0.102 0.00276
Chromium	0.220 0.00021	0.047 0.00248	0.134 0.00135
Copper	351.333 0.342	107.000 5.63	229.167 2.99
Lead	5.717 0.00557	0.148 0.00779	2.947 0.00668
Nickel	0.357 0.00035	0.176 0.00927	0.267 0.00481
Selenium	<0.005 <0.00001	0.069 0.00363	<0.037 <0.0018
Silver	0.055 0.00005	0.026 0.00137	0.041 0.00071
Thallium	<0.104 <0.00010	0.041 0.00216	<0.073 <0.0011
Zinc	7.067 0.00688	0.045 0.00237	3.556 0.00463

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(1) Data from three daily grab samples. Cuprous chloride wastewater.
(2) Copper carbonate wastewater.

Section 5 of this report describes the methodology of the sampling program. In the Copper Salts Subcategory, a total of six days of sampling were conducted at two plants. Six different wastewater streams were sampled and analyzed. The evaluation of toxic pollutants in these streams was based on 234 data points for toxic metals and 678 data points for toxic organics. In Table 13-5, toxic metal pollutant raw wastewater data are presented as average daily concentrations and loads for the two sampled plants.

POLLUTION ABATEMENT OPTIONS

Toxic Pollutants of Concern

The major toxic pollutant of concern in the Copper Salts Subcategory is copper. Other toxic metals found in significant concentrations in process wastewaters are probably related to the purity of the raw materials used. Antimony, arsenic, and nickel occurred in process wastewaters from two of the sampled plants, while lead and zinc were found at significant concentrations at only one plant. No toxic organics were found in significant concentrations. Antimony, arsenic, copper, lead, nickel, and zinc were also found at significant concentrations in raw waste during screening and verification sampling at a copper sulfate plant during Phase I (see the Phase I Development Document).

When impure raw materials are used, toxic metal impurities are removed in the purification process through filtration or washing of the product. These pollutants then occur in wastewater or as solid wastes. Using pure raw materials, which are not always available or economical, however, can often allow recycle of most or all of the process wastewater.

Existing Control and Treatment Practices

Treatment and control practices conducted at plants that were visited during this program were previously described. Presented below are brief descriptions of treatment practices at other plants producing copper salts.

Plant F115 produces copper carbonate. Process wastewaters are treated in a system using alkaline precipitation, sedimentation, and final pH adjustment prior to discharge to surface waters.

Plant F108 manufactures cuprous chloride by direct reaction of copper and chlorine. No process wastewater is generated or discharged from this process.

Plant F132 produces copper chloride by direct reaction of copper and chlorine. Process wastewaters, which consist of only air scrubber blowdown are treated in a system using sedimentation, and filtration. These treated wastewaters are recycled to the air scrubber.

Plant F116 produces copper iodide by direct reaction of copper and iodine. The only source of process wastewater is the air scrubber, and all air scrubber water is recycled with no blowdown.

Other Applicable Control and Treatment Technologies

Alkaline precipitation and clarification will remove copper and most other toxic metals found in copper salts process wastes. Filtration of the effluent from this treatment process would further reduce metals and solids. Three of four direct dischargers are currently using this technology or its equivalent.

Process Modifications and Technology Transfer Options

One of the major sources of process wastewater in the subcategory is copper carbonate washwater. The copper carbonate precipitate which must be washed results from addition of soda ash to a copper salt solution, usually copper sulfate. The washwater is of relatively high pH (approximately pH 8-9) and typically contains low concentrations of most toxic metals. Optimum removal of copper occurs at a pH of 8.5 to 9.0, however, elevated concentrations of copper may occur in the wastewater in suspended form. The application of Level 2 technology (sand or multi-media filtration) at this point may produce a suitable quality effluent without application of Level 1. Increased product yield (copper carbonate) would result from the wastewater treatment system by recovery of the copper carbonate from the filter.

A reduction in the volume of process contact wastewater generated might be achieved by:

1. Recycling of scrubber water or use of scrubber water as make-up for product solutions, where possible;

2. Minimizing product changes by careful product scheduling, or, for multi-product facilities, by increasing the number of reactors. This can result in reducing the volume of washdown water required by minimizing product changeover.

As shown on Table 13-3, all four plants with scrubbers are recycling the scrubber water. Product scheduling is a management perogative subject to customer demands. Consequently, the Agency has not identified any technology which would provide significant reduction in water use in this industry.

Sludge volumes may be reduced by the use of caustic soda instead of lime. This practice offers other advantages including reduced scale formation and faster reaction times.

Best Management Practices

The best technology for the treatment of scrubber wastewater from copper salts production is recycle, where technically feasible. Implementation of this technology requires installation of piping and pumping as needed. Scrubber liquors may be used as process makeup. All four plants with air scrubbers are recycling the scrubber liquor.

If contact is possible with leakage, spillage of raw materials or product, all storm water and plant site runoff should be collected and directed to the plant treatment facility. This contamination can be minimized by indoor storage of chemicals, proper air pollution control, and elimination of spills.

All other contact wastewater including leaks, spills, and washdowns should be contained and treated.

If solids from the wastewater treatment plant are disposed or stored on-site, provision should be made to control leachates and permeates. Leachates and permeates which contain toxic pollutants should be directed to the treatment system for further treatment.

Advanced Technology

No demonstrated advanced technology was identified for this subcategory.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1

Level 1 treatment consists of alkaline precipitation, clarification or settling, and final pH adjustment of the effluent if necessary. Sludges generated are dewatered in a filter press. As part of the treatment system, a holding basin sized to retain 4-6 hours of influent is provided as a safeguard in the event of treatment system shutdown. The treatment technology is illustrated in Figure 10-10.

The initial treatment step is the addition of caustic soda. This is followed by clarification/settling (if the wastewater characteristics are suitable, a tube settler may be substituted for a clarifier to conserve space). Sludge is removed from the clarifier and directed to a filter press for dewatering. Pits are provided at the filter press for the temporary storage of sludge. The sludge is periodically transported to a hazardous material landfill. Filter press filtrate is returned to the head of the treatment system.

The pH of the treated wastewater stream is adjusted to an acceptable level by acid addition prior to discharge if necessary. A monitoring system is installed at the discharge point. The objective of Level 1 technology is to remove heavy metals and suspended solids.

B. Level 2

Level 2 treatment consists of granular media filtration for further removal of metal hydroxide precipitates and other solids from the wastewater. This technology is portrayed in Figure 10-11. In practice, when Level 2 technology is added to Level 1, final pH adjustment would be reconfigured to occur after filtration not prior to it. The objective of Level 2 treatment technology in this subcategory is to achieve, at a reasonable cost, more effective removal of toxic metals than provided by Level 1. Filtration will both increase treatment system solids removal and decrease the variation in solids removal exhibited by typical clarifier performance. Four facilities in this subcategory practice filtration of copper salts wastewater, including three of four direct dischargers.

Level 2 treatment was selected as the basis for BPT because it represents a typical and viable industry practice for the control of suspended solids, copper and nickel. Three of the four direct dischargers have Level 2 treatment already installed. One of the five indirect dischargers also has Level 2 installed. In addition, level 2 technology was the basis for the promulgated copper sulfate BPT and BAT effluent limitations. Six plants currently do not discharge copper salts process wastewater, and will not incur additional costs for treatment.

As discussed under "Process Modifications and Technology Transfer Options" in this Section, copper carbonate wastewater may be amenable to Level 2 treatment without first practicing Level 1 treatment. The benefits to this approach would include increased recovery of copper carbonate product, a reduction in cost of treatment, and a reduction in discharge of toxic metals to receiving waters.

Equipment for Different Treatment Levels

A. Equipment Functions

Conventional sludge dewatering by a filter press is used for sludge generated by the clarification/settling system. In some cases, the sludge may be amenable to copper recovery. However, off-site disposal in compliance with RCRA Subtitle C regulations is generally assumed. If a tube settler is used instead of a clarifier, backwash from the settler is returned to the influent holding basin. Solids resulting from Level 2 filter backwash would be handled as discussed in item C (Solids Handling) below. All equipment is conventional and readily available.

B. Chemical Handling

Caustic soda (50 percent NaOH) is used to precipitate heavy metals in Level 1. At all levels of treatment, sulfuric acid (concentrated) may be used to reduce the pH of the treated wastewater prior to discharge.

C. Solids Handling

Treatment sludges generated by Level 1 are dewatered in a filter press. The solids may be disposed of off-site or processed for copper recovery. Level 2 filter backwash may be sent to the head of the plant or, if the solids concentration is sufficiently high, may be sent directly to the filter press.

Treatment Cost Estimates

Based upon copper salt subcategory profile characteristics, two model plants were selected for costing of Level 1 and Level 2 treatment systems. The overall ranges of production and wastewater flow have been discussed earlier in this section and summarized in Table 13-1. Since copper carbonate production accounts for a large portion (>90 percent) of the process wastewater generated in the subcategory, one set of model plant wastewater flow characteristics are based upon flow attributable to this product, and a separate model plant has been established for the other copper salts.

Estimates of material usages for both treatment levels in the copper salts segment are listed below:

Chemical	Amount	Level
NaOH (50 percent sol.)	3.0 kg/day	1
H_2SO_4 (100 percent)	0.08 kg/day	1

Estimates of solid waste generated for both treatment levels in the copper salts segment are provided below:

Waste Source	Amount
Level 1 sludge	0.0176 m^3/day
Level 2 sludge	0.0018 m^3/day

Flow data for copper salts producers is presented in Table 13-3. The flow for copper salts plants exclusive of copper carbonate is very close to the flow from copper sulfate plants. The pollutants are the same, and are at similar levels. Therefore, the Agency has combined the copper salts subcategory with the copper sulfate subcategory. The model plant for all copper salts exclusive of copper carbonate has an annual production of 85.2 metric tons (the average of the plants reporting production in Phase II) and a daily wastewater flow of 0.8 cubic meters calculated from the daily production and the unit flow of 0.94 m^3/kkg (as found at copper sulfate plants) with an operating schedule of 102 days per year. These characteristics were used as the basis for treatment cost estimates at all levels.

For the copper carbonate industry, the unit flow is the average flow from all three plants reporting flow data. The average production rate and operating days for the plants reporting these data are used for the model plant. Therefore, the model plant has an annual production of 155 metric tons and a daily wastewater flow of 291 cubic meters. The unit flow is 58.1 m^3/kkg with an operating schedule of 31 days per year. These characteristics were used as the basis for treatment cost estimates at all levels.

Estimates of material usages for both treatment levels in the copper carbonate subgroup are listed below:

Chemical	Amount	Level
NaOH (50 percent sol.)	87.3 kg/day	1
H_2SO_4 (100 percent sol.)	29.1 kg/day	1

Estimates of solid waste generated for both treatment levels in the copper carbonate subgroup are listed below:

TABLE 13-6. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Copper Salts Subgroup

ANNUAL PRODUCTION: 85.2 METRIC TONS

DAILY FLOW: 0.8 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2	3	4	5
Facilities	0.7				
Installed Equipment (Including Instrumentation)	6.6	0.4			
Engineering	1.5	0.1			
Contractor Overhead and Profit	1.3	0.1			
Contingency	1.0	0.1			
Land					
Total Invested Capital	11.1	0.7			
Annual Capital Recovery	1.8	0.1			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	6.3	0.2			
Residual Waste Disposal	0.7	0.1			
Total Annual Cost	8.8	0.4			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, pH adjustment

LEVEL 2: Filtration

TABLE 13-7. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Copper Carbonate Subgroup

ANNUAL PRODUCTION: 155 METRIC TONS

DAILY FLOW: 291 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2	3	4	5
Facilities	25.4				
Installed Equipment (Including Instrumentation)	163.7	31.3			
Engineering	37.8	6.3			
Contractor Overhead and Profit	34.0	5.6			
Contingency	26.1	4.3			
Land					
Total Invested Capital	287.0	47.5			
Annual Capital Recovery	46.7	7.7			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	78.3	9.3			
Residual Waste Disposal	0.9	0.1			
Total Annual Cost	125.9	17.1			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, sludge dewatering, pH adjustment

LEVEL 2: Filtration

Waste Source	Amount
Level 1 sludge	0.058 m^3/day
Level 2 sludge	0.006 m^3/day

Model Plant Treatment Costs

On the basis of the model plant specifications and design concepts presented earlier and in Section 10, the estimated cost of treatment for the model plant with two treatment levels are shown in Tables 13-6 and 13-7. The cost of Level 2 is incremental to Level 1.

Basis for Regulations

Basis for BPT Limitations

A. Technology Basis

For BPT, the Agency is setting limitations based upon alkaline precipitation, clarification, granular media filtration, dewatering of the sludge in a filter press and final pH adjustment of the effluent (if necessary). Three of the four direct dischargers have Level 2 treatment. One of the five indirect dischargers also has Level 2 installed. All copper sulfate plants have this technology or its equivalent installed. Six plants currently do not discharge copper salts process wastewater, and will not incur additional costs for treatment.

B. Flow Basis

For the copper salts segment of the Copper Salts Subcategory, a unit flow rate of 0.94 m^3/kkg was selected as representative. This flow rate was derived as described above under model plant treatment costs. The unit flow is the same as for copper sulfate.

For the copper carbonate segment of the Copper Salts Subcategory, a unit flow of 58.1 m^3/kkg was selected as being representative of the group. This flow rate was derived as described above under model plant treatment costs.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are being established is based on an evaluation of the raw wastewater data from screening and verification sampling in Phase I and Phase II, consideration of the raw materials used in the process, literature data, historical discharge monitoring reports and discharge permit applications, and the treatability of the toxic pollutants.

Tables 8-1 through 8-14 summarize the achievable concentrations of toxic metal pollutants from the literature using available technology options, information from other industries, and treatability studies. Water use and discharge data are presented earlier in this section together with generalized process characteristics. Pollutant concentrations of raw wastewater streams and a summary of maximum concentrations observed of toxic pollutants detected during screening and verification sampling at several plants are also presented earlier in this section. Data from Appendix A on the performance of in-place industry treatment systems were also utilized in developing the list of pollutants to be regulated.

The following parameters were selected initially as candidate toxic pollutants for BPT regulations: copper, nickel, lead and zinc. These pollutants were observed at least once during screening and verification sampling at concentrations considered treatable. A number of other priority pollutant metals were detected during screening and verification sampling, however, concentrations were generally less than 0.3 mg/l. Arsenic and selenium were also considered as toxic pollutants to be regulated.

During Phase I, significant concentrations of arsenic were found at a copper sulfate facility during screening and verification sampling. However, arsenic was not selected as a regulated pollutant in Phase I, because it will be controlled by the technology selected for control of the other toxic metal pollutants. For the same reason, arsenic was also rejected as a regulated pollutant in Phase II.

Selenium was also found during Phase I screening and verification sampling in a treated effluent. However, selenium was not found in the raw wastewater. The maximum concentration of selenium found in a combined raw wastewater influent to treatment during Phase II screening and verification sampling was 0.14 mg/l.

Consideration of the raw wastewater concentrations presented earlier in this section, wastewater information obtained from industry and from Phase I, and information presented in Section 8 on the effectiveness of hydroxide precipitation, clarification, and filtration suggested a reduction in the number of parameters to be regulated. Copper, nickel, and selenium were selected as the toxic pollutants to be regulated. Since selenium was found in Phase I in treated effluent but not the raw waste, selenium was selected for regulation in Phase I, along with copper and nickel, to assure that excessive amounts of selenium were not discharged after treatment.

Control of the regulated parameters, copper, nickel and selenium, will provide adequate control for arsenic, lead and zinc; therefore no limitations are set for these three parameters.

D. Basis of BPT Pollutant Limitations

Limitations are presented as both concentrations (mg/l) and loads (kg/kkg), and the relationship between the two is based on the unit flow rates of 0.94 m^3/kkg for copper salts and 58.1 m^3 for copper carbonate. BPT limitations, which apply to all process wastewater discharged, are presented in Table 13-8 and 13-9.

1. Conventional Pollutants

a. pH

The treated effluent is to be controlled within the range of 6.0 - 9.0. This limitation is based upon the data presented in Appendix B of the Development Document for Proposed Effluent Guidelines for Phase I Inorganic Chemicals (Ref. 1) and the JRB study (Ref. 2).

b. TSS

The BPT limitations for TSS are based upon the limitations promulgated for the copper sulfate industry in Phase I. The long-term average of 20 mg/l was used to develop discharge limitations. Variability factors of 1.2 for a monthly average and approximately 3.6 for a 24-hour maximum were used yielding TSS concentration limitations of 24 mg/l and 73 mg/l respectively. Thus, utilizing these values, one obtains TSS mass limitations for the Copper Salts subcategory of:

1. Copper Salts Segment

30-day average:

$(24\ mg/l)(0.94\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.023\ kg/kkg$

24-hour maximum:

$(73\ mg/l)(0.94\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$

= 0.069 kg/kkg

2. Copper Carbonate Segment

30-day average:

(24 mg/l)(58.1 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 1.4 kg/kkg

24-hour maximum:

(73 mg/l) (58.1 m^3/kkg) (kg/10^6 mg)(1000 l/m^3)
= 4.2 kg/kkg

2. Toxic Pollutants

a. Copper

The BPT limitations for copper are based on the limitations promulgated in Phase I for copper sulfate manufacture. During Phase I, a long-term average concentration of 0.89 mg/l copper was derived, and estimated variability factors of 1.2 and 3.6 were used to compute the 30-day average and 24-hour maximum values of 1.1 and 3.2 mg/l respectively.

Utilizing these values, mass limitations for the Copper Salts Subcategory may be obtained as follows:

1. Copper Salts Segment

30-day average:

(1.1 mg/l)(0.94 m^3/kkg)(kg/10^6 mg)(1000 l/m$_3$)
= 0.0010 kg/kkg

24-hour maximum:

(3.2 mg/l)(115 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.0030 kg/kkg

2. Copper Carbonate Segment

30-day average:

(1.1 mg/l)(58.1 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.064 kg/kkg

24-hour maximum:

$(3.2 \text{ mg/l})(58.1 \text{ m}^3\text{/kkg})(\text{kg}/10^6\text{mg})(1000 \text{ l/m}^3)$
$= 0.19$ kg/kkg

b. Nickel

The BPT limitations for nickel are based on the limitations promulgated in Phase I for copper sulfate manufacture. In Phase I, a long-term average concentration of 1.8 mg/l nickel was derived, and estimated variability factors of 1.2 and 3.6 were used to compute the 30-day average and 24-hour maximum values of 2.1 and 6.4 mg/l respectively.

The mass limitations for nickel in the Copper Salts Subcategory were derived as follows:

1. Copper Salts Segment

30-day average:

$(2.1 \text{ mg/l})(0.94 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.0020$ kg/kkg

24-hour maximum:

$(6.4 \text{ mg/l})(0.94 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.0060$ kg/kkg

2. Copper Carbonate Segment

30-day average:

$(2.1 \text{ mg/l})(58.1 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.12$ kg/kkg

24-hour maximum

$(6.4 \text{ mg/l})(58.1 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.37$ kg/kkg

c. Selenium

The BPT limitations for selenium are based on the limitations promulgated in Phase I for copper sulfate manufacture. During Phase I, a long-term average concentration of 0.44 mg/l selenium was derived, and estimated variability factors of 1.2 and 3.6 were used to compute the 30-day average and 24-hour maximum values of 0.53 and 1.6 mg/l respectively.

Utilizing these values, mass limitations for the Copper Salts Subcategory may be obtained as follows:

1. Copper Salts Segment

30-day average:

(0.53 mg/l)(0.94 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.00050 kg/kkg

24-hour maximum:

(1.6 mg/l)(0.94 m^3/kkg)(kg/10^6)(1000 l/m^3)
= 0.0015 kg/kkg

2. Copper Carbonate Segment

30-day average

(0.53 mg/l)(58.1 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.031 kg/kkg

24-hour maximjm

(1.6 mg/l)(58.1 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.093 kg/kkg

Basis for BCT Effluent Limitations

On October 29, 1982, EPA proposed a revised BCT methodology. While EPA is considering revising that proposed methdology, in this subcategory no additional technologies were identified which would remove significant additional quantities of conventional pollutants. Accordingly, EPA has determined that BCT equals BPT in this subcategory. As a result, BCT for TSS is equal to the BPT limitations.

Basis for BAT Effluent Limitations

Application of Advanced Level Treatment

For BAT, the Agency is promulgating limitations based on treatment consisting of Level 2 (BPT) technology. Toxic

TABLE 13-8. BPT EFFLUENT LIMITATIONS FOR COPPER SALTS

Coventional Pollutants	Long-Term(1) Avg.(mg/l)	VFR(1)	Conc. Basis(1) (mg/l) 30-day avg.	Conc. Basis(1) (mg/l) 24-hr. max.	Effluent Limit(1) (kg/kkg) 30-day avg.	Effluent Limit(1) (kg/kkg) 24-hr. max.
TSS(2)	20	1.2/3.6	24	73	0.023	0.069
Toxic Pollutants						
Copper(3)	0.89	1.2/3.6	1.1	3.2	0.0010	0.0030
Nickel(3)	1.8	1.2/3.6	2.1	6.4	0.0020	0.0060
Selenium(3)	0.44	1.2/3.6	0.53	1.6	0.00050	0.0015

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the copper sulfate subcategory in Phase I.
(2) Also applicable to NSPS and BCT.
(3) Also applicable to BAT and NSPS.

TABLE 13-9. BPT EFFLUENT LIMITATIONS FOR COPPER CARBONATE

Conventional Pollutants	Long-Term(1) Avg. (mg/l)	VFR(1)	Conc. Basis(1) (mg/l)		Effluent Limit (kg/kkg)	
			30-day avg.	24-hr. max.	30-day avg.	24-hr. max.
TSS(3)	20	1.2/3.6	24	73	1.4	4.2
Toxic Pollutants						
Copper(2)	0.89	1.2/3.6	1.1	3.2	0.064	0.19
Nickel(2)	1.8	1.2/3.6	2.1	6.4	0.12	0.37
Selenium(2)	0.44	1.2/3.6	0.53	1.6	0.031	0.093

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the copper sulfate subcategory in Phase I.

(2) Also applicable to BAT and NSPS.

(3) Also applicable to NSPS and BCT.

TABLE 13-10. BAT EFFLUENT LIMITATIONS FOR COPPER SALTS

Toxic Pollutants	Long-Term[1] Avg. (mg/l)	VFR[1]	Conc. Basis[1] (mg/l) 30-day avg.	Conc. Basis[1] (mg/l) 24-hr. max.	Effluent Limit[1] (kg/kkg) 30-day avg.	Effluent Limit[1] (kg/kkg) 24-hr. max.
Copper	0.89	1.2/3.6	1.1	3.2	0.0010	0.0030
Nickel	1.8	1.2/3.6	2.1	6.4	0.0020	0.0060
Selenium	0.44	1.2/3.6	0.53	1.6	0.00050	0.0015

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the copper sulfate subcategory in Phase I.

TABLE 13-11. BAT EFFLUENT LIMITATIONS FOR COPPER CARBONATE

Toxic Pollutants	Long-Term(1) Avg. (mg/l)	VFR(1)	Conc. Basis(1) (mg/l)		Effluent Limit (kg/kkg)	
			30-day avg.	24-hr. max.	30-day avg.	24-hr. max.
Copper	0.89	1.2/3.6	1.1	3.2	0.064	0.19
Nickel	1.8	1.2/3.6	2.1	6.4	0.12	0.37
Selenium	0.44	1.2/3.6	0.53	1.6	0.031	0.093

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the copper sulfate subcategory in Phase I.

pollutants limited by the BAT regulation are copper, nickel and selenium at the same concentration levels and loadings established for BPT. No other technology which would remove significant additional amounts of pollutants is known.

A. Technology Basis

Alkaline precipitation followed by clarification and filtration, dewatering of the sludge in a filter press, followed by pH adjustment (if necessary) form the selected BAT technology basis (same as BPT).

B. Flow Basis

Unit wastewater flow rates of 0.94 m^3/kkg of copper salts and 58.1 m^3/kkg of copper carbonate have been selected for BAT (same as BPT).

C. Selection of Pollutants to be Regulated

Toxic Pollutants

The toxic pollutants copper, nickel, and selenium have been selected at the same concentration levels and loadings proposed for BPT. Tables 13-10 and 13-11 present the BAT limitations for the Copper Salts Subcategory.

Basis for NSPS Effluent Limitations

For NSPS, the Agency is promulgating limitations equal to BAT since no additional technology which would remove significant additional amounts of pollutants is known. The pollutants limited include pH, TSS, copper, nickel, and selenium which are listed in Table 13-8 and 13-9.

Basis for Pretreatment Standards

The Agency is promulgating PSES and PSNS that are equal to BAT limitations because BAT provides better removal of copper, nickel and selenium than is achieved by a well operated POTW with secondary treatment installed and therefore these pollutants would pass through the POTW in the absence of pretreatment. The promulgated PSES and PSNS for copper sulfate are also based on the BAT technology. Pollutants regulated under PSES and PSNS are copper, nickel, and selenium.

Using the summary data presented in Tables 13-5 and 13-8, and the data from Phase I, the Agency has estimated the percent removal for copper and nickel by comparing the untreated waste concentrations for those two toxic metals with the treated waste concentrations for the selected BAT technology for those same two pollutants. The untreated waste concentrations presented below are an average of the concentrations found for copper sulfate during Phase I and for those copper salts plants sampled in Phase II. This is a reasonable approach since many plants make copper sulfate and other copper salts and combine the wastewater streams for treatment. The calculation of the percent removals for copper and nickel is as follows:

Copper: Raw Waste = 1175 mg/l
BAT = 0.89 mg/l

Percent Removal = [(1175 - 0.89) ÷ (1175)] (100)
= 99.9%

Nickel: Raw Waste = 51.2 mg/l
BAT = 1.8 mg/l

PercentRemoval = [(51.2 - 1.8) ÷ (51.2)] (100)
= 96.5%

The percent removals are greater than the removals achieved for copper (58%) and nickel (19%) by 25% of the POTWs in the "50 Cities" study (Fate of Priority Pollutants in Publicly Owned Treatment Works, Final Report, EPA 440/1-82/303, September, 1982). Therefore, since the BAT technology achieves a greater percent removal of copper and nickel than is achieved by a well-operated POTW with secondary treatment, those two toxic metals would pass through a POTW in the absence of pretreatment.

Selenium has also been selected for regulation under PSES for the reasons previously given for its selection for regulation under BAT.

Existing Sources

There are currently five indirect discharging copper salts plants in the subcategory. There is also one indirect discharge copper sulfate plant. For Pretreatment Standards for Existing Sources (PSES), the Agency is promulgating limitations based on BAT described above. The pollutants limited are copper, nickel, and selenium as presented in Table 13-8 and 13-9.

New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is setting limitations based on NSPS. Since NSPS is equal to BAT, Tables 13-8 and 13-9 summarize the limitations for the toxic pollutants copper, nickel, and selenium.

SECTION 13

REFERENCES

1. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category," EPA Report No. 440/1-79-007, June 1980.

2. JRB Associates, Inc., "An Assessment of pH Control of Process Waters in Selected Plants," Draft Report to the Office of Water Programs, U.S. Environmental Protection Agency, 1979.

SECTION 14

NICKEL SALTS INDUSTRY

INDUSTRY PROFILE

General Description

The nickel salts covered under this subcategory are nickel sulfate, nickel carbonate, nickel chloride, nickel nitrate, and nickel fluoborate. A process description and discussion of the nickel sulfate industry can be found in the Phase I Development Document: Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-82/007, June, 1982.

Briefly, nickel sulfate is produced by reaction of nickel, nickel oxide or waste nickel (such as spent plating bath) with sulfuric acid:

$$Ni + H_2SO_4 = NiSO_4 + H_2$$

The nickel sulfate may be sold in solution as produced, or may be purified and crystallized before sale as the solid. Detailed process information and the results of screening and verification sampling are provided in the Phase I Development Document. Therefore, the following discussion will cover the other nickel salts covered in this subcategory.

These salts, produced for both captive use and merchant markets, are primarily used in electroplating and catalysts. The chloride salt is most widely used in electroplating, while the carbonate and fluoborate salts are used to a lesser extent. Nickel carbonate is produced from other nickel salts, particularly from nickel sulfate. Upon reduction with hydrogen, nickel carbonate yields a finely divided nickel with good catalytic activity. Nickel nitrate is used in nickel plating, preparation of nickel catalysts, and in manufacture of brown ceramic colors. Tables 1(a) and 1(b) are profile data summaries for the nickel salts subcategory.

There are 12 known facilities manufacturing nickel salts. Two plants have no process wastewater discharge, while six plants discharge directly and four discharge indirectly.

Total annual production of nickel salts is estimated to be in excess of 5,000 metric tons per year and total daily flow is

TABLE 14-1. SUBCATEGORY PROFILE DATA FOR NICKEL SALTS

(a) NICKEL SALTS EXCLUSIVE OF NICKEL SULFATE

Number of Plants in Subcategory	12
Total Subcategory Production Rate	>5000 kkg/yr
Minimum (3 plants)	<4.5 kkg/yr
Maximum	1550 kkg/yr
Total Subcategory Wastewater Discharge	600 m^3/day
Minimum	0
Maximum	195 m^3/day
Types of Wastewater Discharge	
Direct	6
Indirect	4
Zero	2

TABLE 14-1. SUBCATEGORY PROFILE DATA SUMMARY FOR NICKEL SALTS
(b) NICKEL SULFATE(1)

Total Subcategory Capacity Rate(2)	Indeterminant
Total Subcategory Production Rate(2)	6,350 kkg/year
Number of Plants in this Subcategory(3)	11
308 Data on File for	6
With total capacity of	17,700 kkg/year
With total production of	12,650 kkg/year
Representing capacity	NA
Representing production	NA
Plant production range:	NA
Minimum	45 kkg/year
Maximum	5,900 kkg/year
Average production	2,100 kkg/year
Medium production	1,600 kkg/year
Average capacity utilization	71.5
Plant age range:	
Minimum	3
Maximum	48
Waste water flow range	
Minimum	1.5 cubic meters/day
Maximum	17.0 cubic meters/day
Volume per unit product:	
Minimum	0.42 cubic meters/kkg
Maximum	0.72 cubic meters/kkg

---

(1) Source: page 674 of Draft Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-82/007; June 1982.

(2) "Economic Analysis of Proposed Revised Effluent Guidelines and Standards for the Inorganic Chemicals Industry," March, 1980.

(3) Sources of data are Stanford Research Institute, Directory of Chemical Producers, U.S.A., 1977.

NA Not Available

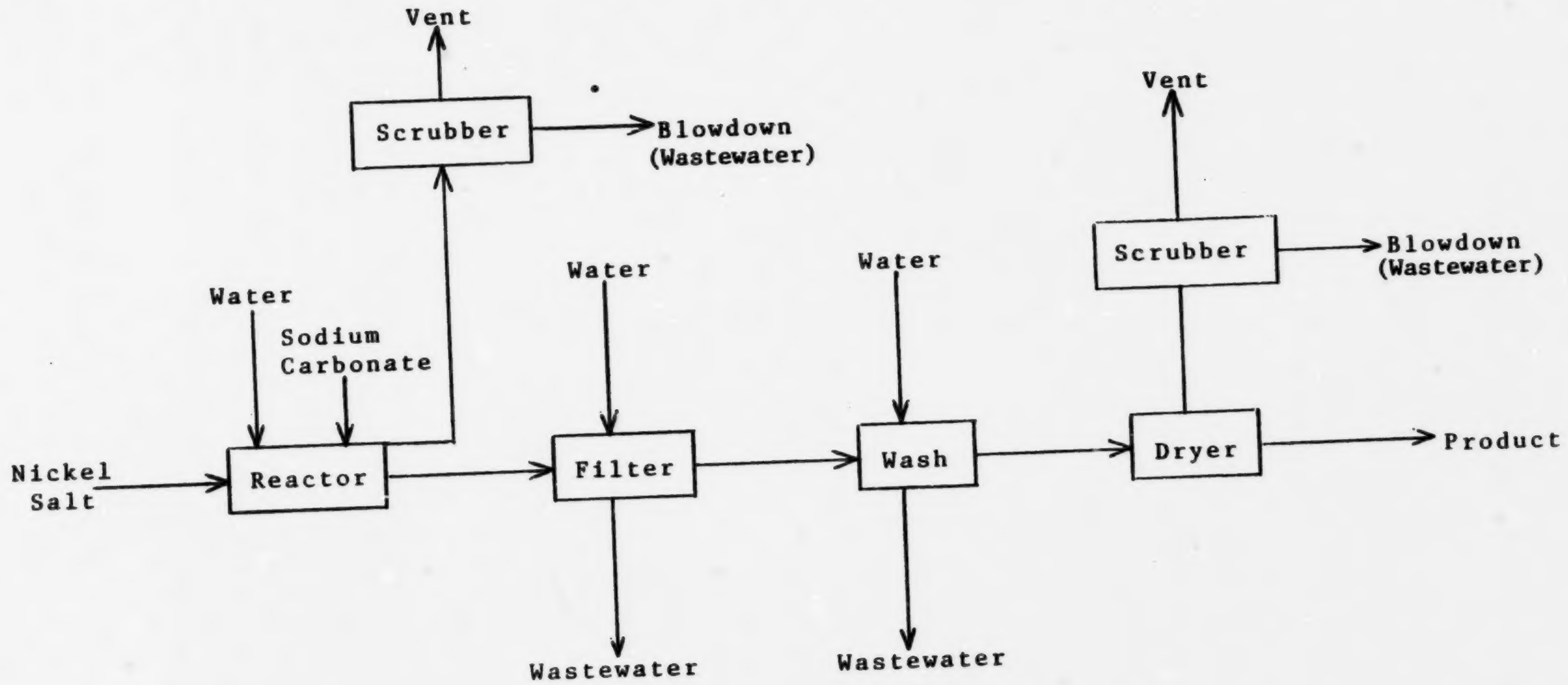

Vent
Scrubber
Blowdown (Wastewater)
Vent
Scrubber
Blowdown (Wastewater)
Water
Sodium Carbonate
Water
Water
Nickel Salt
Reactor
Filter
Wash
Dryer
Product
Wastewater
Wastewater

FIGURE 14-1. GENERALIZED PROCESS DIAGRAM FOR NICKEL CARBONATE.

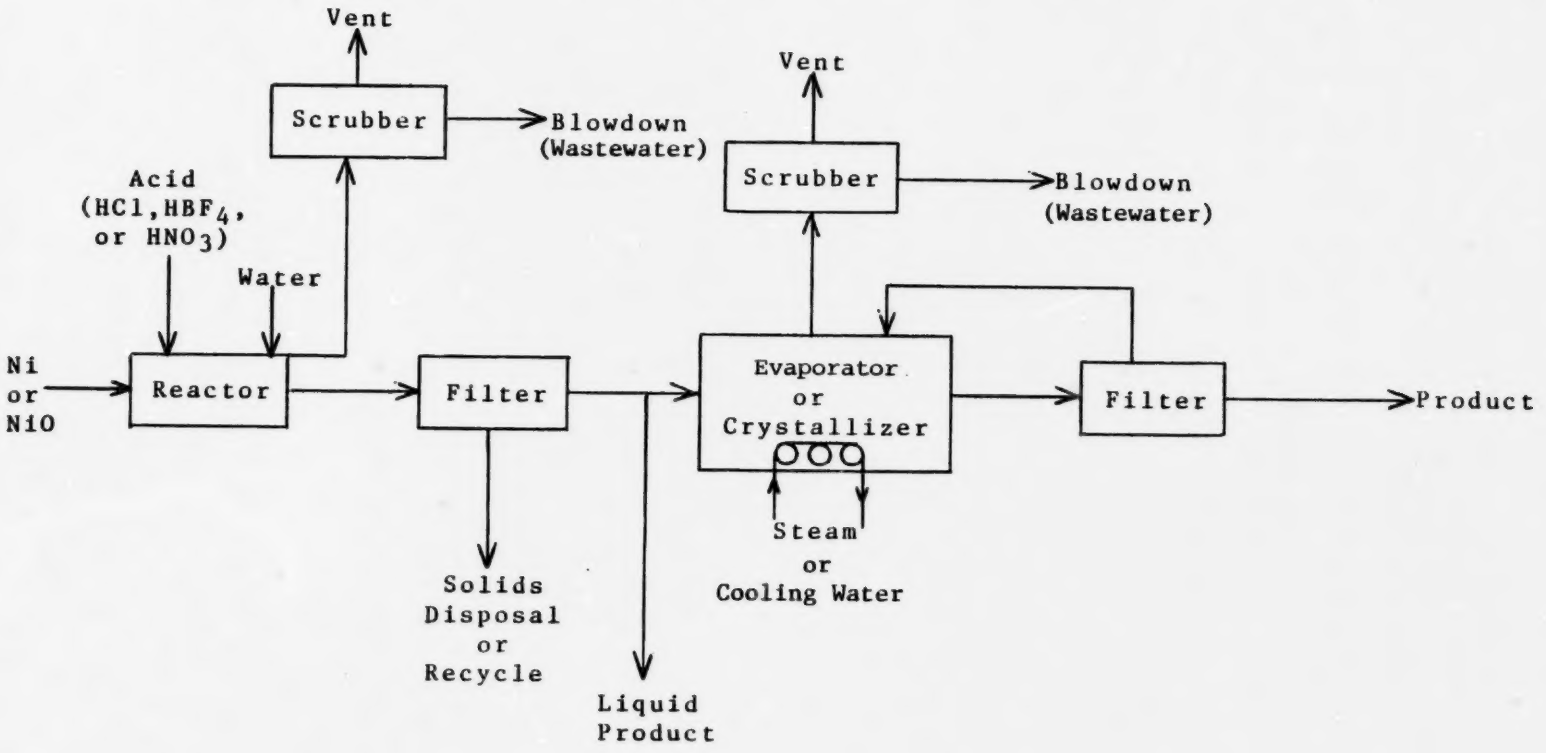

Vent
Scrubber
Blowdown (Wastewater)
Acid (HCl, HBF_4, or HNO_3)
Water
Ni or NiO
Reactor
Filter
Solids Disposal or Recycle
Liquid Product
Vent
Scrubber
Blowdown (Wastewater)
Evaporator or Crystallizer
Steam or Cooling Water
Filter
Product

FIGURE 14-2. GENERALIZED PROCESS FLOW DIAGRAM FOR NICKEL CHLORIDE, NITRATE OR FLUOBORATE.

estimated at greater than 600 cubic meters per day for all plants combined. Based upon available data, it is estimated that over 90 percent of the wastewater flow in the category is generated from nickel carbonate production alone.

General Process Descriptions and Raw Materials

Nickel carbonate is produced by reacting any of several nickel salts with sodium carbonate (soda ash). The general reaction is:

$$NiSO_4 + Na_2CO_3 = NiCO_3 + Na_2SO_4$$

Two different types of raw materials may be used to produce nickel carbonate: pure nickel salts or impure materials such as spent plating solutions. When pure salts are used, the resultant nickel carbonate precipitate is filtered, dried, ground and packaged. When impure sources of nickel are used as raw materials, additional rinsing of the precipitate is necessary to remove impurities. Figure 14-1 presents a general process flow diagram for the manufacture of nickel carbonate.

Other nickel salts, nickel chloride, nickel nitrate, and nickel fluoborate, are produced by reaction of pure nickel or nickel oxides with hydrochloric acid, nitric acid, or fluoboric acid. The general reactions for nickel oxide are:

$$NiO + 2HCl = NiCl_2 + H_2O$$

$$NiO + 2HNO_3 = Ni(NO_3)_2 + H_2O$$

$$NiO + 2HBF_4 = Ni(BF_4)_2 + H_2O$$

The resulting solutions are filtered to remove impurities, crystallized and centrifuged. The pure crystals are then dried, ground and packaged. The products may also be sold as concentrated solutions. Figure 14-2 presents a general process diagram for the manufacture of nickel chloride, nickel nitrate and nickel fluoborate.

WATER USE AND WASTEWATER SOURCES

Water Use

Noncontact cooling water used in the reactors and crystallizers constitutes one of the major water uses in the production of nickel salts. Water is also used in direct process contact as a reaction component and for washing precipitated products. A portion of the reaction water occurs in the product concentrate or in the dry product as its water of hydration, but much of it

TABLE 14-2. WATER USE AT NICKEL SALTS FACILITIES(1)

Water Use	Flow (m^3/kkg of Nickel Salts) Plant Designation								
	F107(2)	F113(2)	F117(2)	F145(2)	F113(3)	F117(3)	F113(4)	F117(4)	F125(4)
Noncontact Cooling	0	0	0	0	10.2	26.8	30.1	33.3	NA
Direct Process Contact	13.6	104	125	7.04	2.86	1.05	5.03	8.35	0.24
Indirect Process Contact	NA	NA	NA	3.52	1.06	NA	2.52	NA	NA
Maintenance	0.28	11.1	NA	7.04	1.06	NA	1.26	NA	NA
Air Pollution Control	NA	0	0	0	---	NA	5.03	0	0.09
Noncontact Ancillary	NA	4.42	NA	70.0	0.53	NA	1.26	NA	NA
TOTALS	13.9	119.5	125	87.6	15.7	27.9	45.2	41.65	0.33

NA Flow volume not available.
--- No information.

(1) Values indicated only for those plants that reported separate and complete information.
(2) Nickel carbonate
(3) Nickel chloride.
(4) Nickel nitrate.

Source: Section 308 Questionnaire and Plant Visit Reports

TABLE 14-3. WASTEWATER FLOW AT NICKEL SALTS FACILITIES(1)

Wastewater Source	Flow (m^3/kkg of Nickel Salts) Plant Designation								
	F107(2)	F113(2)	F117(2)	F145(2)	F113(3)	F117(3)	F113(4)	F117(4)	F125(4)
Direct Process Contact	13.6	104	125	7.04	NA	1.05(5)	NA	0.22	NA
Indirect Process Contact	NA	---	NA	3.52	0	NA	1.56	NA	NA
Maintenance	0.28	NA	NA	NA	0.98	NA	NA	NA	NA
Air Pollution Control	NA	0	0	NA	---	NA	0.11	0	0.09
TOTALS	13.9	104	125	10.56	0.98	0	1.67	0.22	0.09
Noncontact Cooling	0	0	0	0	10.2	26.8	30.1	33.3	NA
Noncontact Ancillary	NA	15.4	NA	70.0	0.53	NA	1.26	NA	NA

NA Flow volume not available.
--- No information.

(1) Values indicated only for those plants that reported separate and complete information.
(2) Nickel carbonate
(3) Nickel chloride.
(4) Nickel nitrate.
(5) Wastewater recycled within plant.

Source: Section 308 Questionnaire and Plant Visit Reports is evaporated to the atmosphere. Small amounts of water are used for maintenance purposes, and several plants use water in scrubbers for dust or fume control. Table 14-2 presents a summary of available plant data on water use.

Wastewater Sources

Noncontact Cooling Water

Noncontact cooling is one of the major sources of discharged water. This stream is usually not contaminated and is not treated before discharge.

Direct Process Contact

Plants which use impure nickel raw materials generate filter sludges or wash wastes which must be treated before discharge. Filter sludges and decants from processes using pure raw materials are often recycled back to the process. In nickel carbonate production, direct contact process wastewater from washing impurities from the nickel carbonate is the major source of process wastewater.

Maintenance

Equipment and area cleaning wastes, and indirect contact wastewater such as spills and sump leaks are periodic streams that account for a small amount of wastewater generated by the production of nickel salts. For most nickel salts, including nickel sulfate but not including nickel carbonate, this is the major source of process wastewater.

Air Pollution Control

Wet scrubbers are frequently used to control the discharge of fumes from reaction tanks and evaporators or concentrators. Blowdown from these scrubbers may be intermittent or continuous.

The available data concerning wastewater flows at nickel salts facilities is summarized in Table 14-3. It is observed that the nickel carbonate processes produce substantially more process wastewater than do other nickel salts processes. This difference is attributable to the greater quantities of wash water required for removal of product impurities in the nickel carbonate production process.

DESCRIPTIONS OF PLANTS VISITED AND SAMPLED

Six plants producing nickel salts were visited during this study. In addition, wastewater sampling was conducted at three of these plants. This section presents summary descriptions of facilities visited and sampled during this program.

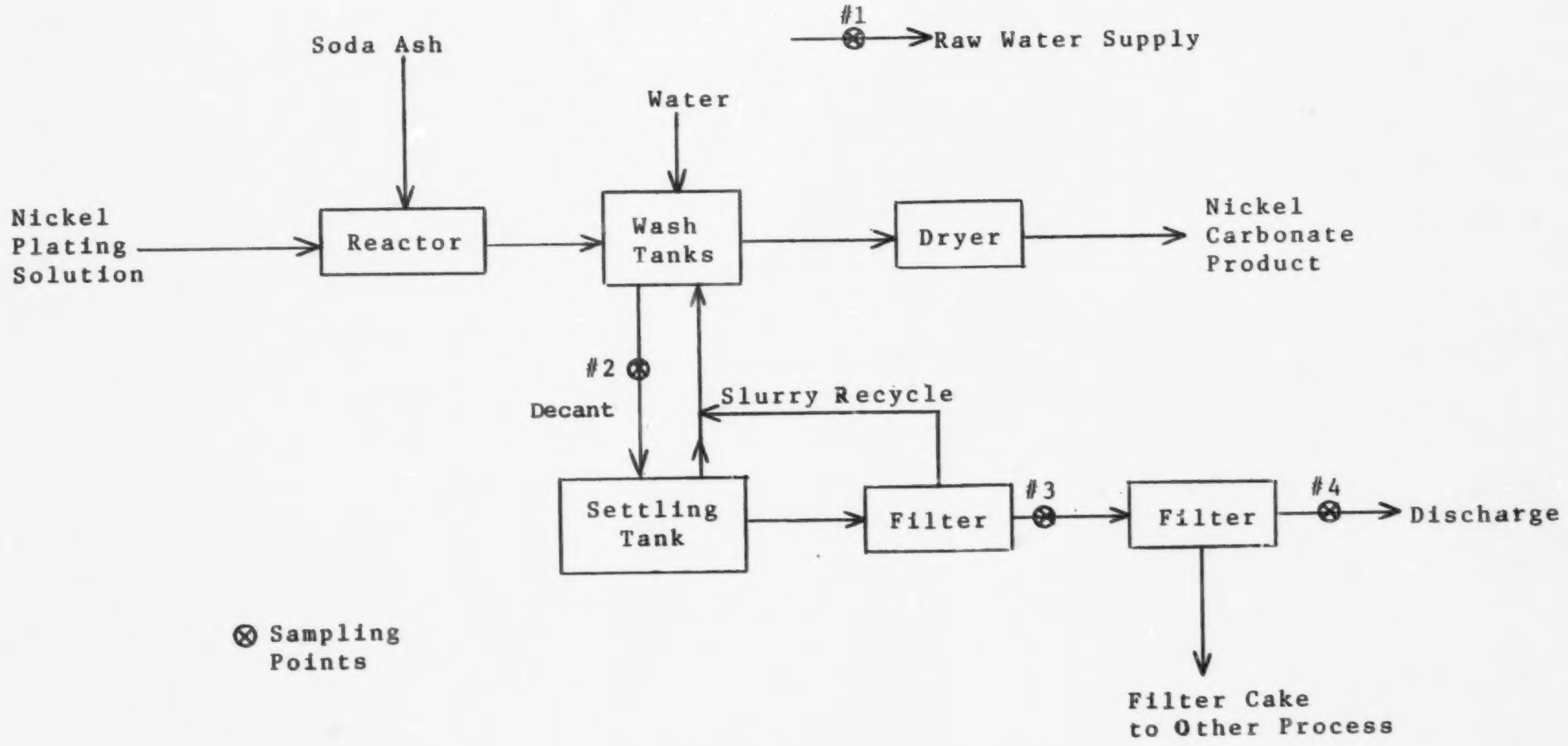
Plants Sampled

Plant F113 produces nickel carbonate, nickel chloride, nickel nitrate and other inorganic salts. During the sampling visit, only the nickel carbonate process was operating. Nickel carbonate is produced on a batch basis by reacting a spent plating solution with soda ash. After reaction, the precipitate is rinsed to remove impurities, then dried and packaged. The decanted rinse water passes through two filter presses. The filter cake is recovered and returned to the process and the filtrate is discharged. Other sources of wastewater include washdown, pump seal leaks, and spills. All wastewater from this plant is discharged to a POTW without pretreatment. Figure 14-3 is a diagram of the process showing sampling points. Table 14-4 presents data on the major pollutant concentrations and loads for the sampled streams.

Plant F117 produces nickel carbonate, nickel chloride, nickel nitrate, nickel fluoborate, and a variety of other metal salts. During the plant visit, only the nickel carbonate process was sampled. Nickel carbonate is produced by reacting nickel sulfate with soda ash. The resultant slurry is passed through a vacuum filter. The filter cake is washed with water to remove impurities, then dried, milled and packaged. The washwater is treated in a nickel recovery system which uses caustic addition to pH 10, sand filtration, with final pH adjustment with sulfuric acid addition before discharge to surface waters. Solids captured in the sand filter are subjected to filter press filtration for nickel recovery. Fluoride-containing wastewater from nickel fluoborate production, when it occurs, is combined with other process wastewater for treatment by lime neutralization, flocculant addition, clarification, and final pH adjustment. Figure 14-4 is a diagram of the process and treatment system showing sampling points. Table 14-4 presents data on the major pollutant concentrations and loads for the sampled streams.

Plant F107 produces nickel carbonate, nickel nitrate and several other inorganic salts. Both nickel carbonate and nickel nitrate processes were operating during the sampling visit. Nickel carbonate is produced by a proprietary batch process. Washdown wastes, spills and filter backwash from this process are collected in a trench with other process wastewaters and are discharged to a POTW without treatment. Nickel nitrate is

NICKEL CARBONATE



#1
Raw Water Supply
Soda Ash
Water
Nickel Plating Solution
Reactor
Wash Tanks
Dryer
Nickel Carbonate Product
#2
Decant
Slurry Recycle
Settling Tank
Filter
#3
Filter
#4
Discharge
Filter Cake to Other Process
⊗ Sampling Points

FIGURE 14-3. PROCESS AND SAMPLING LOCATIONS FOR PLANT F113.

NICKEL CARBONATE

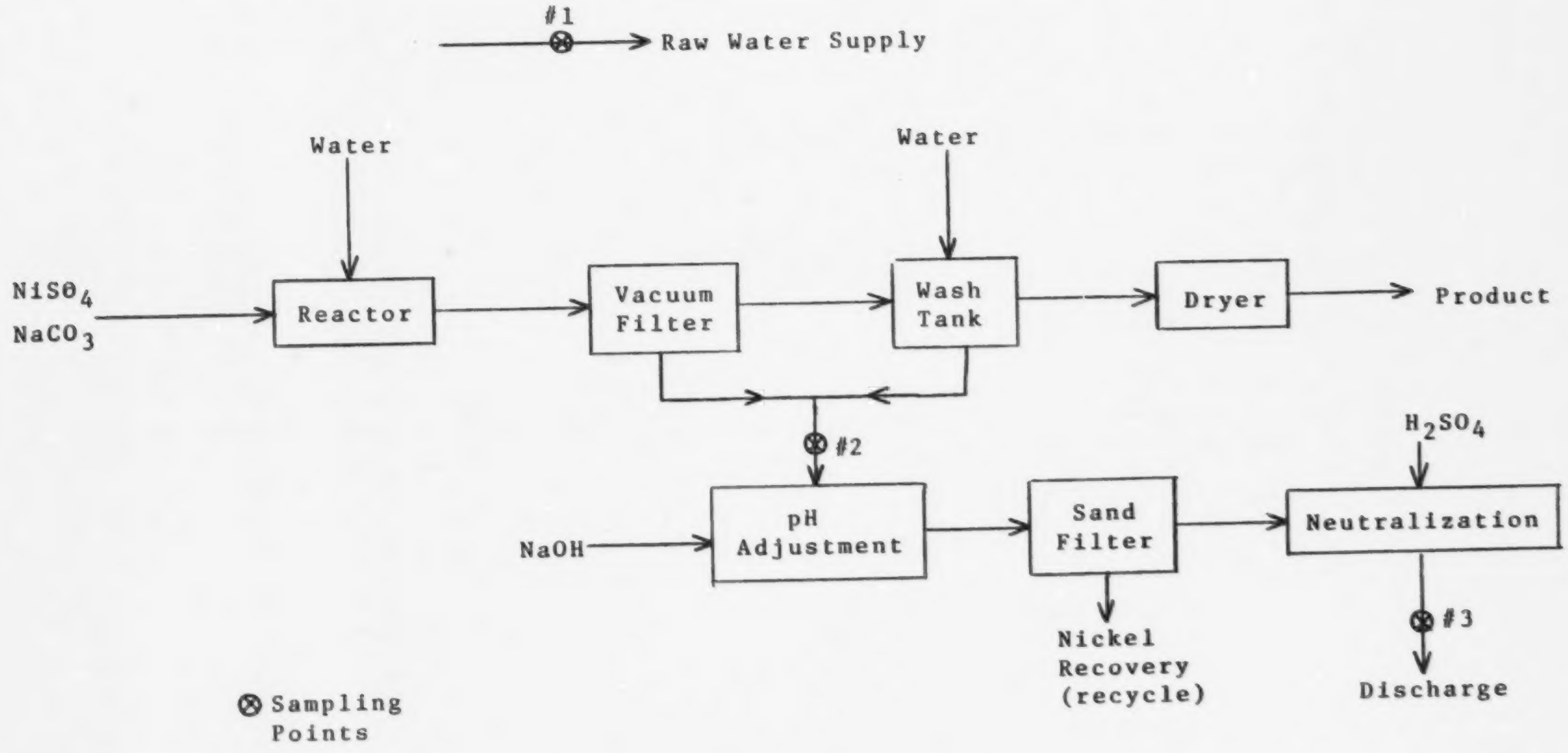

#1
Raw Water Supply
Water
Water
$NiSO_4$
$NaCO_3$
Reactor
Vacuum Filter
Wash Tank
Dryer
Product
#2
H_2SO_4
NaOH
pH Adjustment
Sand Filter
Neutralization
#3
Nickel Recovery (recycle)
Discharge
Sampling Points

FIGURE 14-4. PROCESS, WASTEWATER TREATMENT, AND SAMPLING LOCATIONS FOR PLANT F117.

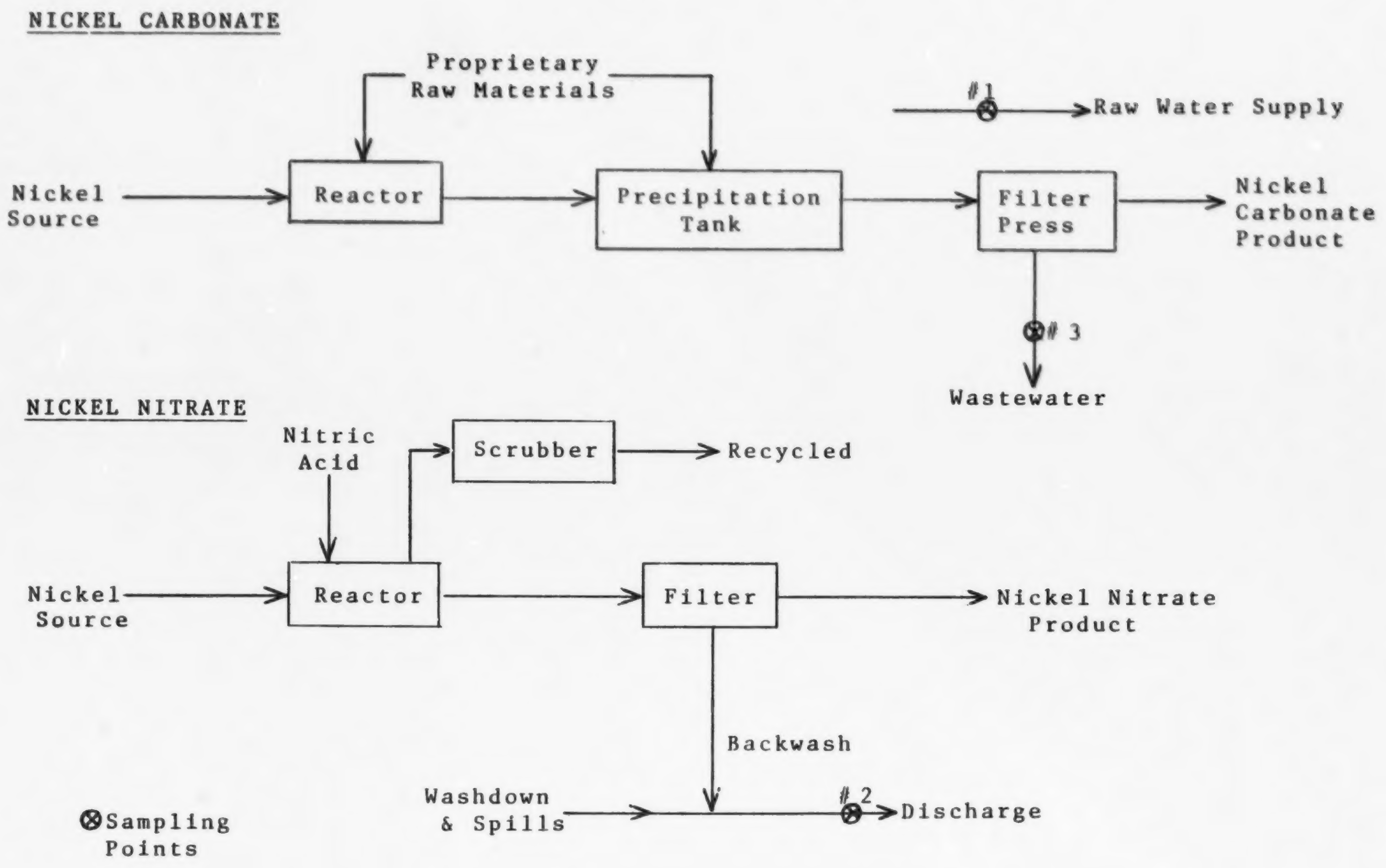

NICKEL CARBONATE
Proprietary Raw Materials
Nickel Source
Reactor
Precipitation Tank
#1
Raw Water Supply
Filter Press
Nickel Carbonate Product
#3
Wastewater
NICKEL NITRATE
Nitric Acid
Scrubber
Recycled
Nickel Source
Reactor
Filter
Nickel Nitrate Product
Backwash
Washdown & Spills
#2
Discharge
⊗ Sampling Points

FIGURE 14-5. PROCESS AND SAMPLING LOCATIONS FOR PLANT F107.

produced at this plant by a process similar to that described previously. Figure 14-5 is a diagram of the two processes showing sampling points. Table 14-4 presents data on the major pollutant concentrations and loads for the sampled streams.

Other Plants Visited

Plant F145 produces nickel carbonate, nickel chloride, and nickel nitrate salts in addition to many other chemicals. Manufacturing processes for the nickel salts are similar to those previously described. Scrubber wastes, washings, filtrates, tank cleanouts, and leaks or spills which cannot be recycled are sent to a central treatment system where all plant wastewaters are treated. Treatment consists of equalization, lime precipitation, clarification and sludge dewatering. Overflow from this system is then treated by biological treatment prior to discharge.

Plant F119 produces nickel carbonate and nickel nitrate in addition to numerous other inorganic salts. Processes for the nickel salts are similar to those previously described. Off-gases from the nitrate production are exhausted through a condenser to recover nitric acid, and the gases are then incinerated to destroy nitrogen oxides before release to the atmosphere. Process wastewaters from all products manufactured are directed to a central treatment system consisting of pH adjustment, settling, flocculation, clarification, and sludge dewatering. The clarifier overflow is discharged to a POTW.

Plant F118 produces nickel carbonate and nickel chloride in addition to many other inorganic compounds. Wastewater streams from all chemical processes are combined and passed through a treatment system consisting of equalization, alkaline precipitation, clarification and final pH adjustment before discharge.

Plants F113, F117, F145, and F118 also produce nickel sulfate. The nickel sulfate process wastewaters are combined with other nickel process wastewaters for treatment and discharge.

Summary of Toxic Pollutant Data

Nine toxic metals were found at detectable concentrations in the total raw wastewater at the three sampled plants. The table below presents the maximum daily concentrations observed for these pollutants found in the total process raw wastewater:

TABLE 14-4. POLLUTANT CONCENTRATIONS AND LOADS FOR SAMPLED NICKEL SALTS FACILITIES(1)

Stream No.	Stream Description	TSS	Ni	Sb	Cu
		$\frac{mg/l}{kg/kkg}$			
		Plant F113 $(NiCO_3)$			
1.	Supply Water	<1.0 ---	0.017 ---	0.008 ---	0.017 ---
2.	Rinse Decant	10.0 ---	7.03 ---	1.00 ---	0.042 ---
3.	Filtered Decant	12.8 0.907	3.47 0.246	0.60 0.043	0.019 0.00135
4.	Effluent	35.3 2.50	16.6 1.18	0.67 0.0475	0.025 0.0018
		Plant F117 $(NiCO_3)$			
1.	Supply Water	<0.5 ---	0.36 ---	<0.005 ---	0.008 ---
2.	Raw Wastewater	10.0 2.53	41.0 10.39	0.057 0.0144	0.024 0.0061
3.	Treated Effluent	12.1 3.07	0.54 0.137	0.029 0.0074	0.031 0.0079
		Plant F107			
1.	Supply Water	7 ---	3.20 ---	0.029 ---	0.041 ---
2.	Ni Nitrate Wastewater(2)	160 ---	805 ---	1.16 ---	7.35 ---
3.	Ni Carbonate Wastewater	370 ---	560 ---	<0.54 ---	0.26 ---

--- Insufficient information.

(1) Flow and concentration values are average values for three days, except where noted.

(2) Two-day sampling.

Pollutant	Maximum Concentration Observed (ug/l)
Antimony	1,545
Cadmium	1,513
Chromium	170
Copper	877
Lead	170
Nickel	1,513,000
Silver	82
Thallium	300
Zinc	698

Section 5 of this report describes the methodology of the sampling program. In the Nickel Salts Subcategory, a total of nine days of sampling were conducted at these plants. Seven different process wastewater streams were sampled and analyzed. The evaluation of toxic pollutants in these streams was based on 260 data points for toxic metals and 791 data points for toxic organics. In Table 14-5, toxic pollutant raw waste data are presented as average daily concentrations and loads for the three sampled plants.

POLLUTION ABATEMENT OPTIONS

Toxic Pollutants of Concern

The toxic pollutants of concern in the Nickel Salts Subcategory are nickel and copper. Other toxic metals found in significant concentrations in process wastewaters are related to the purity of the raw materials used. Antimony and thallium occurred in process wastewater at concentrations greater than 100 ug/l from two of the sampled plants, while cadmium and zinc were found at significant concentrations at only one plant. No toxic organics were found in significant concentrations. Nickel, copper, antimony, cadmium, and zinc were also found in untreated process wastewater during the Phase I screening and verification sampling at three nickel sulfate plants.

When impure raw materials are used, toxic metal impurities will be removed in the purification process through filtration or washing of the product. These pollutants can then occur in wastewater or solid wastes. Using pure raw materials, which are not always available or economical, however, can often allow recycle of the process water.

Existing Wastewater Control and Treatment Practices

TABLE 14-5. TOXIC POLLUTANT RAW WASTE DATA FOR SAMPLED NICKEL SALTS FACILITIES

Average Daily Pollutant Concentrations and Loads

mg/l
kg/kkg

	Plant Designation			
Pollutant	F113	F117	F107(1)	Overall Average
Antimony	0.673	0.057	<0.531	<0.420
	0.0477	0.014	---	0.0309
Cadmium	<0.010	0.013	<0.850	<0.291
	<0.0007	0.0033	---	<0.002
Chromium	0.073	0.025	0.047	0.048
	0.0052	0.0063	---	0.00575
Copper	0.025	0.024	0.460	0.170
	0.00177	0.0061	---	0.00394
Lead	0.007	0.060	<0.003	<0.023
	0.0005	0.0152	---	0.00785
Nickel	16.6	41.0	540.3	199.3
	1.18	10.4	---	5.79
Silver	0.029	0.008	<0.001	<0.013
	0.0021	0.002	---	0.0021
Thallium	0.118	0.217	<0.003	<0.113
	0.00837	0.0549	---	0.0316
Zinc	0.037	0.023	0.387	0.149
	0.00262	0.0058	---	0.00421

--- Insufficient information.

(1) Flow-proportioned averages from two nickel product wastewater streams.

Treatment and control practices at plants that were visited during this program were previously described. Presented below are brief descriptions of treatment practices at other plants producing nickel salts.

Plant F125 produces nickel nitrate and several other inorganic compounds. Wastewater streams from all processes are treated in a system consisting of equalization, pH adjustment with caustic, and sedimentation in a series of lined and unlined impoundments prior to discharge.

Plant F106 produces nickel chloride and nickel fluoborate in addition to other inorganic compounds. Discharge is to a POTW after pretreatment with lime precipitation and clarification technology.

Plant F139 produces nickel carbonate, nickel chloride, and nickel nitrate salts in addition to other inorganic compounds. Treatment for all process wastewater consists of equalization, sedimentation, neutralization and filter press filtration prior to discharge.

Plant F124 produces nickel nitrate in addition to other inorganic salts. Treatment of process wastewater consists of alkaline precipitation, clarification, filtration and final pH adjustment prior to discharge.

Plant F104 produces nickel chloride and nickel fluoborate and other inorganic chemicals. All products are sold as produced in liquid solution and therefore no wastewater is generated and there is no discharge.

Plant F138 produces nickel fluoborate in small quantities along with a large variety of other inorganic chemicals. No wastewater is generated from the small volume production of nickel fluoborate and therefore there is no discharge.

Other Applicable Control and Treatment Technologies

Alkaline precipitation and clarification will remove nickel and most other toxic metals found in nickel salts process wastes. Several plants are currently using this technology. Other applicable technologies would include filtration of the clarified effluent for further solids and metals removal.

Process Modifications and Technology Transfer Options

One of the major sources of process wastewater in the subcategory is nickel carbonate washwater. The product which must be washed results from addition of soda ash to a nickel salt solution, usually nickel sulfate. The washwater is of relatively high pH (approximately pH 8-10) and typically contains low concentrations of most toxic metals. Nickel concentrations may be elevated in the rinse water, however. Optimum removal of nickel occurs at a pH of 10.2. The application of sand or multimedia filtration at this point could produce a suitable quality effluent at some facilities without other treatment. Increased product yield (nickel carbonate) would result from this technique by recovery of nickel carbonate from the filter backwash. Plants with no current treatment may wish to study this possibility.

A reduction in the volume of process contact wastewater generated might be achieved by:

1. Recycling all direct process contact wastewater or use scrubber water as make-up for product solutions, where possible;

2. Minimizing product changes by careful product scheduling and by increasing the number of reactors. This can result in reducing the volume of washdown water required by minimizing product changeover.

As shown in Tables 14-2 and 14-3, both plants with scrubber wastewater have minimized the discharge of process wastewater. Plant F113 recycles over 90% of its scrubber water, while Plant F125 has eliminated all other sources of process wastewater discharges except the scrubber water. Product scheduling is a management perogative suject to customer demand. The agency has not identified any additional technology which could be applied to significantly reduce the volume of wastewater discharges in this subcategory.

Best Management Practices

The best technology for the treatment of scrubber wastewater from nickel salts production is recycle, where technically feasible. Implementation of this technology requires installation of piping and pumping as needed. Scrubber liquors may be usable as process makeup.

If contact is possible with leakage, spillage of raw materials or product, all storm water and plant site runoff should be collected and directed to the plant treatment facility. This contamination can be minimized by indoor storage of chemicals, proper air pollution control and elimination of spills.

All other contact wastewater including leaks, spills, and washdowns should be contained and treated.

If solids from the wastewater treatment plant are disposed or stored on-site, provision should be made to control leachates and permeates. Leachates and permeates which contain toxic pollutants should be directed to the treatment system for further treatment.

Plant F117, which produces a variety of inorganic chemicals (including all four Phase II nickel salts), practices segregation and commingling of various wastewater streams depending upon chemical characteristics. Some wastewater, particularly that originating from nickel carbonate and nickel sulfate production, is combined and treated in the same wastewater treatment facility and the treatment sludge is recovered to reclaim its nickel whereas other streams like the nickel nitrate wastewater is commingled with cobalt nitrate wastewater for treatment. Segregation of wastewater may at some facilities enable lower concentrations of toxic metals to be attained or may allow increased product yield by recovery of product from treatment sludges.

Advanced Technology

For facilities using impure raw materials such as plating solutions, etc., significant concentrations of a variety of toxic metals may be present in wastewater, particularly in dissolved form. Careful control of pH to reduce the solubility of the metals followed by clarification and filtration may be necessary for optimum treatment.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1

Level 1 treatment consists of alkaline precipitation, clarification or settling, and final pH adjustment of the effluent if necessary. Sludges generated are dewatered in a filter press. As part of the treatment system, a holding basin sized to retain 4-6 hours of influent is provided as a safeguard in the event of treatment system shutdown. The treatment technology is illustrated in Figure 10-10.

The initial treatment step is the addition of caustic soda. This is followed by clarification/settling (if the wastewater characteristics are suitable, a tube settler may be substituted for a clarifier to conserve space). Sludge is removed from the clarifier and directed to a filter press for dewatering. Pits are provided at the filter press for the temporary storage of sludge. The sludge is periodically transported to a hazardous material landfill. Filter press filtrate is returned to the head of the treatment system.

The pH of the treated wastewater stream is adjusted to an acceptable level by acid addition prior to discharge if necessary. A monitoring system is installed at the discharge point. The objective of Level 1 technology is to remove heavy metals and suspended solids.

B. Level 2

Level 2 treatment consists of granular media filtration for further removal of metal hydroxide precipitates and other solids from the wastewater. This technology is portrayed in Figure 10-11. In practice, when Level 2 technology is added to Level 1, final pH adjustment would occur after filtration not prior to it. The objective of Level 2 treatment technology in this subcategory is to achieve, at a reasonable cost, more effective removal of toxic metals than provided by Level 1. Filtration will both increase treatment system solids removal and decrease the variation in solids removal exhibited by typical clarifier performance. Four facilities in this subcategory have Level 2 or its equivalent, including four of the six direct dischargers. Level 2 technology was the basis for the promulgated BPT, BCT, and BAT effluent limitations and NSPS, PSES, and PSNS for the nickel sulfate subcategory.

As discussed under "Process Modifications and Technology Transfer Options" in this section, nickel carbonate wastewater may be amenable to Level 2 treatment without first practicing Level 1 treatment. The benefits to this approach would include increased recovery of nickel carbonate product and a reduction in treatment costs.

Equipment for Different Treatment Levels

A. Equipment Functions

Conventional sludge dewatering by a filter press is used for sludge generated by the clarification/settling system. In some cases, the sludge may be amenable to nickel recovery, however, off-site disposal in a hazardous material landfill is generally assumed. If a tube settler is used instead of a clarifier, backwash from the settler is returned to the influent holding basin. Solids resulting from Level 2 filter backwash would be handled as discussed in item C (Solids Handling) below. All equipment is conventional and readily available.

B. Chemical Handling

Caustic soda (50 percent NaOH) is used to precipitate heavy metals in Level 1. At all levels of treatment, sulfuric acid (concentrated) may be used to reduce the pH of the wastewater prior to discharge.

C. Solids Handling

Treatment sludges generated by Level 1 are dewatered in a filter press. The solids may be disposed of off-site in a hazardous material landfill or processed for nickel recovery. Level 2 filter backwash may be sent to the head of the plant or, if the solids concentration is sufficiently high, may be sent directly to the filter press.

Treatment Cost Estimates

Based upon Nickel Salt Subcategory profile characteristics, two model plants were selected for costing of Level 1 and Level 2 treatment systems. The overall ranges of production and wastewater flow have been discussed earlier in this section and summarized in Table 14-1. Since nickel carbonate production accounts for a large portion (>90 percent) of the process wastewater generated in the subcategory, one set of model plant wastewater flow characteristics are based upon flow attributable to this product, and a second model plant has been established for the other nickel salts.

Flow data for nickel salts producers is presented in Table 14-3. The flow for nickel salts plants exclusive of nickel carbonate is very close to the flow from nickel sulfate plants (See the Phase I Development Document). The pollutants are the same, and are at similar levels. Therefore, the Agency has combined the nickel salts subcategory with the nickel sulfate subcategory.

The model plant for all nickel salts exclusive of nickel carbonate has an annual production of 429 metric tons (the average of the plants reporting production in Phase II) and a daily wastewater flow of 1.67 cubic meters calculated from the daily production and the unit flow of 0.68 m^3/kkg (as found at nickel sulfate plants) with an operating schedule of 175 days per year. These characteristics were used as the basis for treatment cost estimates at all levels.

TABLE 14-6. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Nickel Salts Subgroup

ANNUAL PRODUCTION: 429 METRIC TONS

DAILY FLOW: 1.67 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2	3	4	5
Facilities	1.1				
Installed Equipment (Including Instrumentation)	12.2	0.4			
Engineering	2.7	0.1			
Contractor Overhead and Profit	2.4	0.1			
Contingency	1.8	0.1			
Land					
Total Invested Capital	20.2	0.7			
Annual Capital Recovery	3.3	0.1			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	7.4	0.2			
Residual Waste Disposal	0.5	Negl.			
Total Annual Cost	11.2	0.3			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, pH adjustment

LEVEL 2: Filtration

TABLE 14-7. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Nickel Carbonate Subgroup

ANNUAL PRODUCTION: 142 METRIC TONS

DAILY FLOW: 94.8 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2	3	4	5
Facilities	11.7				
Installed Equipment (Including Instrumentation)	122.9	22.5			
Engineering	26.9	4.5			
Contractor Overhead and Profit	24.2	4.1			
Contingency	18.6	3.1			
Land					
Total Invested Capital	204.3	34.2			
Annual Capital Recovery	33.2	5.6			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	56.8	7.5			
Residual Waste Disposal	0.3	Negl.			
Total Annual Cost	90.3	13.1			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, sludge dewatering, pH adjustment

LEVEL 2: Filtration

For the nickel carbonate industry, the average production rate and operating days for the plants reporting these data are used for the model plant. Therefore, the model plant has an annual production of 142 metric tons and a daily wastewater flow of 94.8 cubic meters. The unit flow is 120 m^3/kkg with an operating schedule of 179 days per year. These characteristics were used as the basis for treatment costs at all levels. The unit flow is the average (to two significant figures) of Plants F113 and F117. Plant F107 was not included because nickel carbonate is produced for captive used and the additional cleaning water use at F113 and F117 is not done at Plant F107. Plant F145 was not used because the plant uses pure raw materials to produce a reagent grade product, and it also does not have the additional cleaning steps necessary at the average plant.

Estimates of material usages for both treatment levels for the nickel salts segment are listed below:

Chemical	Amount	Level
NaOH (50 percent sol.)	2.34 kg/day	Level 1
H_2SO_4 (100 percent)	0.17 kg/day	Level 1

Estimates of solid waste generated for all treatment levels for the nickel salts segment are provided below:

Waste Source	Amount
Level 1 sludge	0.012 m^3/day
Level 2 sludge	0.001 m^3/day

Estimates of material usage for all three treatment levels in the nickel carbonate segment are listed below:

Chemical	Amount	Level
NaOH (50 percent sol.)	53.0 kg/day	Level 1
H_2SO_4 (100 percent)	9.8 kg/day	Level 1

Estimates of solid waste generated for all treatment levels are provided below:

Waste Source	Amount
Level 1 sludge	0.019 m^3/day
Level 2 sludge	0.0019 m^3/day

Model Plant Treatment Costs

On the basis of model plant specifications and design concepts presented earlier and in Section 10, the estimated costs of treatment for two model plants with two treatment levels are shown in Tables 14-6 and 14-7. The cost of Level 2 is incremental to Level 1.

Basis for Regulations

Basis for BPT Limitations

A. Technology Basis

For BPT, the Agency is setting limitations based upon alkaline precipitation, clarification, dewatering of the sludge in a filter press, filtration, and final pH adjustment of the effluent (if necessary). Four of the six direct dischargers have Level 2 treatment installed. Two plants currently have no discharge of nickel salts process wastewater, and will not incur additional costs for treatment. Level 2 was the technology basis for the promulgated effluent limitations guidelines and standards for the nickel sulfate subcategory.

B. Flow Basis

For the nickel salts segment of the Nickel Salts Subcategory, a unit flow rate of 0.68 m^3/kkg was selected as being representative of the group. This flow rate was derived as described above under model plant treatment costs.

For the nickel carbonate segment of the Nickel Salts Subcategory, a unit flow of 120 m^3/kkg was selected as being representative of the group. This flow rate was derived as described above under model plant treatment costs.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are being established is based on an evaluation of the raw wastewater data from screening and verification sampling, consideration of the raw materials used in the process, literature data, historical discharge monitoring reports and discharge permit applications, and the treatability of the toxic pollutants.

Tables 8-1 through 8-14 summarize the achievable concentrations of toxic metal pollutants from the literature using available technology options, information from other industries, and treatability studies. Water use and discharge data are presented earlier in this section together with generalized process characteristics. Pollutant concentrations of raw wastewater streams and a summary of maximum concentrations observed of toxic pollutants detected during sampling at several plants are also presented earlier in this section. Data from Appendix A on the performance of in-place industry treatment systems were also utilized in developing the list of pollutants to be regulated.

The following parameters were selected initially as candidate toxic pollutants for BPT regulations: cadmium, copper, chromium, nickel, and zinc. These pollutants were observed at least once during screening and verification sampling at concentrations considered treatable in raw wastewater. However all of the toxics except for nickel were observed at relatively low concentrations in nickel carbonate wastewater. One facility, which was sampled for nickel nitrate wastewater, accounted for numerous observations of significant concentrations of cadmium, copper, chromium and zinc. Nickel concentrations were found at treatable levels at all facilities sampled. A number of other priority pollutant metals were detected during sampling, however, concentrations were generally less than 0.3 mg/l.

Consideration of the raw wastewater concentrations presented earlier in this section, wastewater information obtained from industry in both Phase I and Phase II, and information presented in Section 8 related to the effectiveness of hydroxide precipitation, clarification, and filtration in reducing the amounts of all toxic metals discharged suggested a reduction in the number of parameters to be regulated. Copper and nickel were finally selected as the toxic pollutants to be regulated. Cadmium, chromium, and zinc may occur in some cases at nickel salts facilities (probably associated with some raw material use). However, their occurrence does not appear to be consistent enough to warrant adoption as control parameters for the whole subcategory. In addition, the technology necessary to control copper and nickel will also result in the control of other toxic metals.

D. Basis of BPT Pollutant Limitations

Limitations are presented as both concentrations (mg/l) and loads (kg/kkg), and the relationship between the two is based on the unit flow rates of 0.68 m^3 for nickel salts and 120 m^3/kkg for nickel carbonate. BPT limitations which apply to all process wasteswater discharged, are presented in Tables 14-8 and 14-9..

1. Conventional Pollutants

a. pH

The treated effluent is to be controlled within the range of 6.0 - 9.0. This limitation is based upon the data presented in Appendix B of the Development Document for Proposed Effluent Guidelines for Phase I Inorganic Chemicals and the JRB study.

b. TSS

The BPT limitations for TSS are based upon the BPT limitations promulgated in Phase I for nickel sulfate manufacture. The long-term average of 39.2 mg/l was used to develop discharge limitations. Variability factors of 1.2 for a monthly average and 3.6 for a 24-hour maximum were used yielding TSS concentration limitations of 47 mg/l and 141 mg/l respectively. Thus, utilizing these values, one obtains TSS mass limitations for the Nickel Salts Subcategory of:

1. Nickel Salts Segment

30-day average:

(47 mg/l)(0.68 mm^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.032 kg/kkg

24-hour maximum:

(141 mg/l)(0.68 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.096 kg/kkg

2. Nickel Carbonate Segment

30-day average

(47 mg/l)(120 m^3/kkg)(kg/10^6)(1000 l/m^3)
= 5.6 kg/kkg

24-hour maximum

(141 mg/l)(120 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 17 kg/kkg

2. Toxic Pollutants

a. Nickel

TABLE 14-8. BPT EFFLUENT LIMITATIONS FOR NICKEL SALTS

Conventional Pollutants	Long-Term[1] Avg.(mg/l)	VFR[1]	Conc. Basis[1] (mg/l) 30-day avg.	Conc. Basis[1] (mg/l) 24-hr. max.	Effluent Limit[1] (kg/kkg) 30-day avg.	Effluent Limit[1] (kg/kkg) 24-hr. max.
TSS	39.2	1.2/3.6	47	141	0.032	0.096
Toxic Pollutants						
Nickel	2.5	1.2/3.6	3.0	9.0	0.002	0.006

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the nickel sulfate subcategory in Phase I.

TABLE 14-9. BPT EFFLUENT LIMITATIONS FOR NICKEL CARBONATE

Coventional Pollutants	Long-Term[(1)] Avg. (mg/l)	VFR[(1)]	Conc. Basis[(1)] (mg/l) 30-day avg.	Conc. Basis[(1)] (mg/l) 24-hr. max.	Effluent Limit (kg/kkg) 30-day avg.	Effluent Limit (kg/kkg) 24-hr. max.
TSS	39.2	1.2/3.6	47	141	5.6	17
Toxic Pollutants						
Nickel	2.5	1.2/3.6	3.0	9.0	0.36	1.1

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the nickel sulfate subcategory in Phase I.

The BPT limitations for nickel are based on the BPT limitations promulgated in Phase I for nickel sulfate manufacture. Concentration limitations of 3.0 mg/l (on a monthly basis) and 9.0 mg/l (on a daily basis) were obtained by use of the variability factors of 1.2 for a monthly average and 3.6 for daily maximum computations. Utilizing these values, mass limitations for the Nickel Salts Subcategory may be obtained as follows:

1. Nickel Salts Segment

30-day average:

$(3.0\ mg/l)(0.68\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.002\ kg/kkg$

24-hour maximum:

$(9.0\ mg/l)(0.68\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.006\ kg/kkg$

2. Nickel Carbonate Segment

30-day average

$(3.0\ mg/l)(120\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.36\ kg/kkg$

24-hour maximum

$(9.0\ mg/l)(120\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 1.1\ kg/kkg$

Basis for BCT Effluent Limitations

On October 29, 1982, EPA proposed a revised BCT methodology. While EPA is considering revising that proposed methdology, in this subcategory no additional technologies were identified which would remove significant additional quantities of conventional pollutants. Accordingly, EPA has determined that BCT equals BPT in this subcategory. As a result, BCT for TSS is equal to the BPT limitations.

Basis for BAT Effluent Limitations

Application of Advanced Level Treatment

For BAT, the Agency is promulgating limitations based on treatment consisting of Level 2 technology (same technology as BPT) because we have identified no other technology which would remove significant additional amounts of pollutants. Toxic pollutants limited by the proposed BAT regulation are copper and nickel.

A. Technology Basis

Granular media filtration (Level 2) added to Level 1 has been selected as the basis of BAT (same as BPT).

B. Flow Basis

Unit wastewater flow rates of 0.68 m^3/kkg of nickel salts and 120 m^3/kkg for nickel carbonate has been selected for BAT (same as for BPT).

C. Selection of Pollutants to be Regulated

Toxic Pollutants

The toxic pollutants copper and nickel have been selected for BAT limitation. Tables 14-10 and 14-11 present the BAT limitations for the Nickel Salts Subcategory.

D. Basis of Pollutant Limitations

As in BPT, the BAT limitations are presented as both concentrations (mg/l) and loadings (kg/kkg). Loadings were derived from the calculated concentrations using the model plant flow rates of 0.68 m^3/kkg for nickel salts and 120 m^3/kkg for nickel carbonate.

The BPT effluent limitations for the nickel sulfate subcategory were promulgated May 22, 1975 (40 FR 22402). These effluent limitations were based on Level 2 technology, but there was limited data available to estimate the performance of the technology. Since 1975, long-term treatment system performance data from nickel sulfate manufacturing plants (including one plant manufacturing another Phase II nickel product and treating the combined nickel sulfate and Phase II nickel product process wastewater in the same Level 2 wastewater treatment system) and the agency's treatability study (Treatability Studies for the Inorganic Chemicals Manufacturing Point Source Category, EPA 440/1-80/103, July 1980) shows that the Level 2 technology performs much better than anticipated in 1975. The promulgated BAT effluent limitations for nickel sulfate are based on this better performance. Since the same technology is used at Phase

II nickel salts plants to treat nickel salts wastewaters (including nickel sulfate wastewater in several cases), and since the same pollutants are found at similar levels for nickel salts products, the BAT limitations for the nickel salts subcategory are based on the demonstrated achievable performance of the Level 2 technology.

Toxic Pollutants

a. Copper

The BAT limitations for copper are based on the BAT limitations promulgated in Phase I for nickel sulfate. The long-term average value for copper was 0.3 mg/l and variability factors used were 1.2 for a 30-day average and 3.6 for a 24-hour maximum. The concentration values that are derived using these values are 0.36 mg/l (30-day average) and 1.1 mg/l (24-hour maximum). Mass limitations are computed as follows:

1. Nickel Salts Segment

30-day average:

$(0.36\ mg/l)(0.68\ m^3/kkg)(kg/10^6\ mg)\ (1000\ l/m^3)$
$= 0.00024\ kg/kkg$

24-hour maximum:

$(1.1\ mg/l)(0.68\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.00074\ kg/kkg$

2. Nickel Carbonate Segment

30-day average

$(0.36\ mg/l)(120\ m^3/kkg)(kb/10^6\ mg)(1000\ l/m^3)$
$= 0.042\ kg/kkg$

24-hour maximum

$(1.1\ mg/l)(120\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.13\ kg/kkg$

b. Nickel

TABLE 14-10. BAT EFFLUENT LIMITATIONS FOR NICKEL SALTS

Toxic Pollutants	Long-Term(1) Avg. (mg/l)	VFR(1)	Conc. Basis(1) (mg/l)		Effluent Limit(1) (kg/kkg)	
			30-day avg.	24-hr. max.	30-day avg.	24-hr. max.
Copper	0.3	1.2/3.6	0.36	1.1	0.00024	0.00074
Nickel	0.3	1.2/3.6	0.36	1.1	0.00024	0.00074

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the nickel sulfate subcategory in Phase I.

TABLE 14-11. BAT EFFLUENT LIMITATIONS FOR NICKEL CARBONATE

Toxic Pollutants	Long-Term(1) Avg. (mg/l)	VFR(1)	Conc. Basis(1) (mg/l) 30-day avg.	Conc. Basis(1) (mg/l) 24-hr. max.	Effluent Limit (kg/kkg) 30-day avg.	Effluent Limit (kg/kkg) 24-hr. max.
Copper	0.3	1.2/3.6	0.36	1.1	0.042	0.13
Nickel	0.3	1.2/3.6	0.36	1.1	0.042	0.13

VFR - Variability Factor Ratio

(1) Based upon limitations promulgated for the nickel sulfate subcategory in Phase I.

The BAT limitations for nickel are based upon the BAT limitations promulgated in Phase I for nickel sulfate. The long-term average value for nickel was 0.3 mg/l and the variability factors used were 1.2 for a 30-day average and 3.6 for a 24-hour maximum. The concentrations that are derived using these values are 0.36 mg/l and 1.1 mg/l respectively. Mass limitations are computed as follows:

1. Nickel Salts Segment

30-day average:

$(0.36 \text{ mg/l})(0.68 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.00024$ kg/kkg

24-hour maximum:

$(1.1 \text{ mg/l})(0.68 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.00074$ kg/kkg

2. Nickel Carbonate Segment

30-day average

$(0.36 \text{ mg/l})(120 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.042$ kg/kkg

24-hour maximum

$(1.1 \text{ mg/l})(120 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.13$ kg/kkg

Basis for NSPS Effluent Limitations

For NSPS, the Agency is promulgating limitations equal to BAT since no additional technology which would remove significant additional amounts of pollutants is known to the Administrator. The pollutants limited include pH, TSS, copper and nickel, and the limitations are presented in Tables 14-10 and 14-11.

Basis for Pretreatment Standards

The Agency is promulgating PSES and PSNS that are equal to BAT limitations because BAT provides better removal of copper and nickel than is achieved by a well operated POTW with secondary treatment installed and, therefore, these toxic pollutants would pass through a POTW in the absence of pretreatment. Pollutants regulated under PSES and PSNS are copper and nickel.

Using the summary data presented in Tables 14-5, 14-10, and from Phase I, the Agency has estimated the percent removals of copper and nickel by comparing the untreated waste concentrations for those two toxic metals with the treated waste concentrations for the selected BAT technology for those same two pollutants. The untreated waste concentrations are the average of the raw waste concentrations found for nickel sulfate in Phase I and the raw waste concentrations found at nickel salts plants in Phase II. This approach is reasonable because many plants produce nickel sulfate and other nickel salts and treat the combined wastewaters from those products in the same wastewater treatment system. The calculation of the percent removals is as follows:

Copper: Raw Waste = 27 mg/l
BAT = 0.3 mg/l

Percent Removal = [(27 - 0.3) ÷ (27)](100)
= 98.8%

Nickel: Raw Waste = 343 mg/l
BAT = 0.3 mg/l

Percent Removal = [(343 - 0.3) ÷ (343)] (100)
= 99.9%

The percent removals are greater than the removals achieved for copper (58%) and nickel (19%) by 25% of the POTWs in the "50 Cities" study, (Fate of Priority Pollutants in Publicly Owned Treatment Works, Final Report, EPA 440/1-82/303, September, 1982). Therefore, since the BAT technology achieves a greater percent removal of copper and nickel than is achieved by a well operated POTW with secondary treatment, those two toxic metals would pass through a POTW in the absence of pretreatment.

Existing Sources

There are currently four indirect dischargers in the nickel salts subcategory. For Pretreatment Standards for Existing Sources (PSES), the Agency is promulgating limitations based on BAT described above. The pollutants to be limited are copper and nickel as presented in Tables 14-10 and 14-11.

New Sources

For Pretreatment Standards for New Sources (PSNS), the Agency is setting limitations based on NSPS. Since NSPS is equal to BAT, Tables 14-10 and 14-11 summarize the limitations for the toxic pollutants copper and nickel.

SECTION 14

REFERENCES

1. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category," EPA Report No. 440/1-79-007, June 1980.

2. JRB Associates, Inc., "An Assessment of pH Control of Process Waters in Selected Plants," Draft Report to the Office of Water Programs, U.S. Environmental Protection Agency, 1979.

SECTION 15

SODIUM CHLORATE INDUSTRY

INDUSTRIAL PROFILE

General Description

Most of the sodium chlorate produced (approximately 82 percent) is marketed for use in the conversion to chlorine dioxide bleach in the pulp and paper industry. Sodium chlorate is also used as a chemical intermediate in the production of other chlorates and of perchlorates (7 percent). Agricultural uses (4 percent) of sodium chlorate are as an herbicide, as a defoliant for cotton and as a dessicant in soybean harvesting. Sodium chlorate is used to a lesser extent in the processing of ore (5 percent), the preparation of certain dyes and the processing of textiles, furs, and the manufacture of pyrotechnics. Industry profile data are provided in Table 15-1.

Facilities producing sodium chlorate are usually located at the same site as other facilities such as pulp mills, chlor-alkali plants, and large chemical manufacturing complexes. None of the other Phase II inorganic chemicals are produced at sodium chlorate facilities. Seven of the 13 sodium chlorate plants are located at the same site as chlor-alkali manufacturing facilities.

There are 13 known facilities producing sodium chlorate. Nine facilities are direct dischargers while four facilities achieve zero discharge of process water. There are no indirect dischargers in this subcategory.

The total annual production of sodium chlorate is estimated to be between 250,000 and 300,000 metric tons. In 1981 sodium chlorate production was estimated to be about 274,000 metric tons by the Bureau of the Census.

Total daily discharge from sodium chlorate production is estimated at greater than 17,000 cubic meters (four facilities achieve zero discharge).

General Process Description and Raw Materials

Sodium chlorate is produced by the electrolysis of sodium chloride solution (brine) in diaphragmless electrochemical cells. In older plants, cells with graphite anodes are used while the newer plants are using titanium anodes. Steel cathodes are used

TABLE 15-1. SUBCATEGORY PROFILE DATA FOR SODIUM CHLORATE

Number of Plants in Subcategory	13
Total Subcategory Production Rate	250,000-300,000 kkg/yr
Minimum	2,300 kkg/yr
Maximum	54,000 kkg/yr
Total Subcategory Wastewater Discharge	>17,000 m^3/day
Minimum	0 m^3/day
Maximum	8,180 m^3/day
Types of Wastewater Discharge	
Direct	9
Indirect	0
Zero	4

uniformly across the industry. The overall reaction is as follows:

$$NaCl + 3H_2O = NaClO_3 + 3H_2$$

The brine for the electrolysis may be obtained from natural brines, or rock salt (NaCl) or pure salt may be dissolved in water to produce a brine. The brine is then purified by using sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) to precipitate calcium carbonate and magnesium hydroxide (1). At some facilities, barium chloride ($BaCl_2$) is also added to remove sulfate. The total concentration of calcium plus magnesium should be less than 10 mg/l to prevent fouling of the cathode (1). The brine is filtered to remove the calcium and magnesium precipitates prior to introduction into the cell (1). Sufficient hydrochloric acid is added to maintain the pH of the cell liquor at approximately 6.5. At a higher pH, oxygen evolution increases. At a lower pH, chlorine evolution increases, and both effects are undesirable (1). Noncontact cooling water is used to maintain the temperature of the electrolytic cells between 55°C and 90°C, depending upon the process technology used (1).

Sodium dichromate is added to the electrolytic cells to form a layer of hydrated chromium oxide on the cathode to prevent the following undesirable reactions (1):

$$ClO^- + H_2O + 2e^- = Cl^- + 2\ OH^-$$

$$ClO_3^- + 3\ H_2O + 6e^- = Cl^- + 6\ OH^-$$

The dichromate also acts as a buffer to maintain the pH of the cell at a near optimum value by the following equilibrium reaction (1):

$$Cr_2O_7{}^{--} + H_2O = 2\ CrO_4{}^{--} + 2H^+$$

The sodium dichromate also acts to reduce corrosion of steel surfaces and inhibit the reduction of chlorate and hypochlorite (1). The cell concentration of sodium dichromate ranges from 900 to 5,000 mg/l and approximately 0.5 to 5 kg (1 to 10 lb/ton) of sodium dichromate are consumed per metric ton of product (1,2). Sodium dichromate is added to the electrolytic cells regardless of the type of anode used (graphite or titanium).

Hydrogen and chlorine gas are evolved in the manufacture of sodium chlorate. The chlorine gas is often scrubbed with a sodium hydroxide solution to remove hydrochloric acid and chlorine gas (1). The hydrogen gas is either vented or recovered.

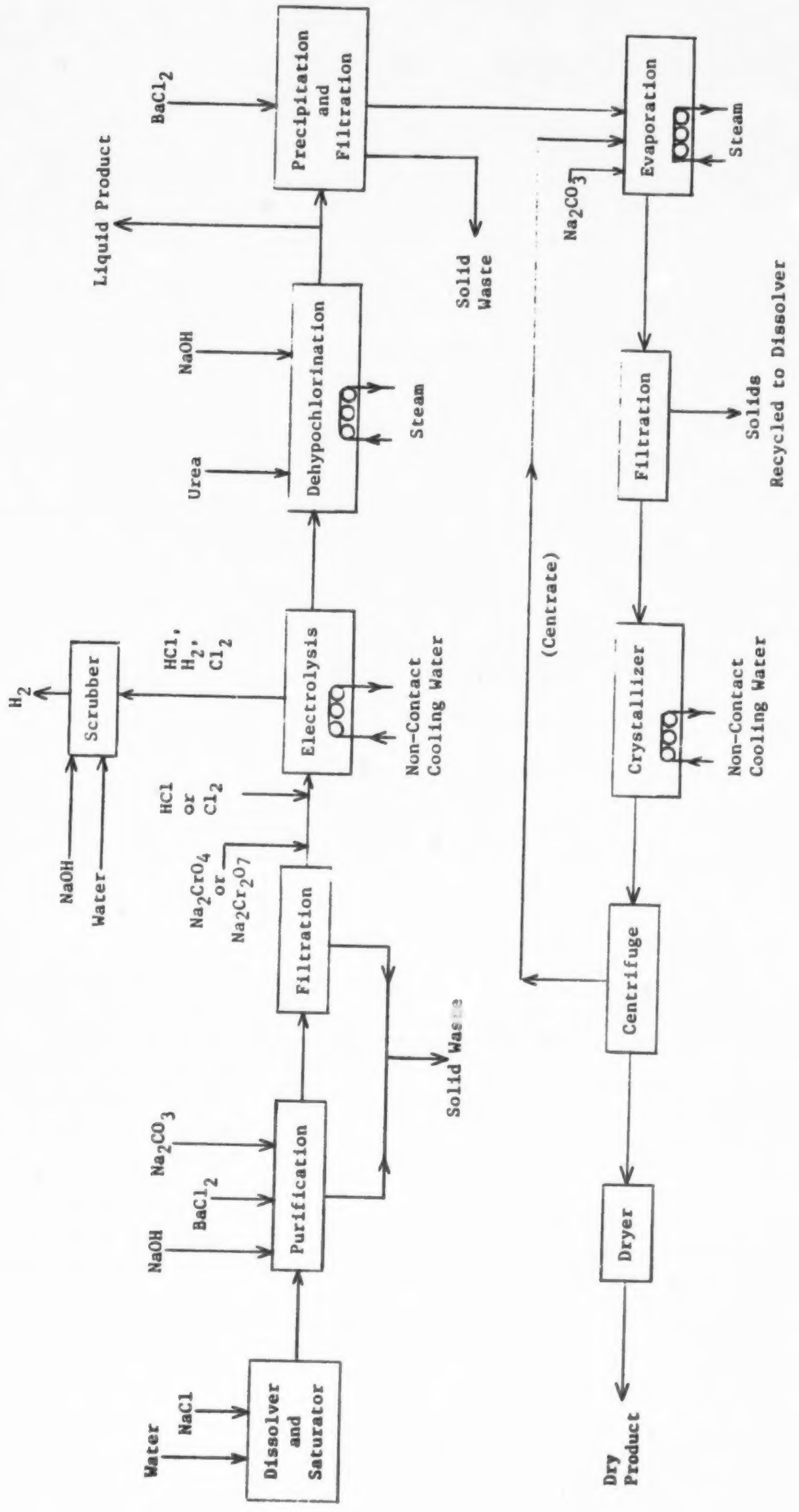

Water
NaCl
Dissolver and Saturator
NaOH
$BaCl_2$
Na_2CO_3
Purification
Solid Waste
Filtration
Na_2CrO_4 or $Na_2Cr_2O_7$
HCl or Cl_2
Electrolysis
Non-Contact Cooling Water
HCl, H_2, Cl_2
Scrubber
H_2
NaOH
Water
Urea
NaOH
Dehypochlorination
Steam
Liquid Product
$BaCl_2$
Precipitation and Filtration
Solid Waste
Evaporation
Na_2CO_3
Steam
Filtration
Solids Recycled to Dissolver
Crystallizer
Non-Contact Cooling Water
Centrifuge
(Centrate)
Dryer
Dry Product

FIGURE 15-1. GENERALIZED PROCESS FLOW DIAGRAM FOR SODIUM CHLORATE

After electrolysis, the sodium chlorate liquor is fed into "dehypo" tanks to destroy residual hypochlorite (dehypochlorination) (1). The hypochlorite is destroyed by a combination of heat (live steam) and chemical reduction (sodium formate, urea, or sodium sulfite). Barium chloride often is added to precipitate the chromate as barium chromate (2). The liquor is then filtered. The filtered liquor may be sold as is, or, if the customer prefers solid sodium chlorate, the filtered liquor is concentrated in an evaporator for crystallization of the product. Soda ash is added to control the pH of the liquor in the evaporator. In the evaporator, the solution is concentrated to precipitate sodium chloride. The vapors are condensed and may become a source of wastewater depending upon the type of condenser used. The liquor is then filtered or allowed to settle to remove sodium chloride from the product. The sodium chloride is returned to the salt dissolver for reuse.

The liquor is cooled to produce sodium chlorate crystals in the crystallizer. The crystals are centrifuged and dried to produce solid sodium chlorate. The centrate is recycled to the evaporator for reuse.

The product is either marketed as a solid or as a solution. Figure 15-1 shows a general process flow diagram for the manufacture of sodium chlorate.

WATER USE AND WASTEWATER SOURCE CHARACTERISTICS

Water Use

Noncontact cooling water is the single largest use of water in the production of sodium chlorate. In addition, water is used in direct process contact as a reaction medium with a portion going into the dry product as its water of crystallization. Plants producing solution-grade sodium chlorate incorporate much of the direct contact process water as the solution water in the product shipped. Small amounts of water are used for maintenance purposes, washdowns, cleanups, filtration, backwashing, etc., and the majority of plants use water in wet scrubbers. Water uses for plants producing sodium chlorate are summarized from industry responses to the Agency's request for information under section 308 of the Act and engineering visit reports in Table 15-2. Table 15-2(a) shows the relationships between type of raw materials, type of product, water use, and discharge status for 11 of the 13 plants in the industry. (Little detailed information is available for the other two plants, as one was being rebuilt, and the other did not have data. Both plants are associated with paper mills).

TABLE 15-2. WATER USAGE AT SODIUM CHLORATE FACILITIES(1)

	Flow (m^3/kkg of Sodium Chlorate)								
	Plant Designation								
WATER USE	F149	F147	F141	F146	F114	F131	F111	F136	F122
Noncontact Cooling	4.08	217.	203.	15.2	331	7.32	79.2	182	NA
Direct Process Contact	0	0.59	1.01	1.61	0.14	1.23	3.59	NA	0
Indirect Process Contact	0.01	NA(2)	NA(2)	2.30	3.31(3)	<0.61	23.2	1.52	NA
Maintenance	0.07	4.12	NA(2)	0.53	0.03	<0.61	7.83	0.08	NA
Air Pollution Scrubbers	0.05	0.62	NA(2)	0.06	0.08	0	0.32	0	NA
Noncontact Ancillary	0	16.5	NA	0.78	0	0	1.86	0	0
TOTALS	4.21	238.8	204.0	20.5	334.6	<9.77	116	183.6	21.7

NA Flow volume not available.
--- No information.

1. Values indicated only for those plants that reported separate and complete information.
2. Included in direct process contact water.
3. In January 1981, no indirect process contact water was used, however a hydrogen compressor was being installed and anticipated to use ring seal water.

Source: Section 308 Questionnaires and Plant Visit Reports

Table 15-2a

Raw Materials, Wastewater Sources, Type of Product, Discharge Status, and unit flows for Sodium Chlorate Plants

PLANT	SALT SOURCE	BRINE PURIF. DISCH.	MAINT. DISCH	BAROM. CONDS.	SCRUB. DISCH.	PROD. FILT.	TYPE PROD.	DISCH.	UNIT FLOW
F112	P. SALT	NO	Recyl	NO	Recyl	N/A	40% Sol.	NO	NA
F141	P. SALT	NO	Recyl	NO	Recyl	Recyl	Solid	NO	(0.93)
F114	P. SALT	NO	Recyl	NO	Recyl	Recyl	Soln.	NO	(0.20)
F131	P. SALT	NO	Recyl	NO	N/A	N/A	Soln.	NO	(1.15)
F149	P. BRIN.	NO	YES	NO	Recyl*	Recyl*	Soln.	YES	0.13
F136	P. BRIN.	NO	Recyl	NO	Recyl **	Recyl	Soln.	YES	1.6
F146	P. BRIN.	Recyl	Recyl	NO	Recyl	Recyl	Soln.	YES	2.3
F122	R. SALT	YES	Recyl	Recyl	Recyl	Recyl	Solid	YES	1.15
F103	R. SALT	YES	YES	Recyl*	YES	Recyl**	Solid	YES	1.22
F147	R. SALT	YES	YES	NO	YES	YES	Solid	YES	4.53
F111	BRINE	YES	YES	YES	YES	YES	Solid	YES	10.15

* Most
** Some

P. Salt = Pure Salt
P. Brin. = Pure Brine
R. Salt = Rock Salt
Recyl = Recycle

Sol or Soln = Solution
NA = Not Available
N/A = Not Applicable
unit flow in m^3/KKG; () = Not discharged

Wastewater Sources

Table 15-3 summarizes flow volumes from wastewater streams in the sodium chlorate industry. Noncontact cooling water which is used to maintain the temperature of the electrolytic cells is the main source of wastewater. This stream is frequently comingled with process wastewater and may or may not be treated prior to discharge. One source of process water stems from purification of the brine fed to the electrolytic cells. Purification of this brine is accomplished by the addition of caustic soda and soda ash to precipitate metal impurities. This purification process results in wastewater produced with the sludge (precipitated metal hydroxides). The purified brine is then electrolyzed in the cells. The cell liquor from the electrolytic cells is filtered and the filter backwash may be a source of process wastewater. The filtered cell liquor following chlorination and electrolysis is partially evaporated to effect crystallization and the resulting slurry is filtered. The mother liquor resulting from the crystallization step is either recycled to brine purification or to the evaporator for further concentration. An additional source of process wastewater includes brine and caustic discharged by air scrubbers which remove HCl and Cl_2 from cell off-gases. Other process wastewater is generated from cell washdown, filter bag wash, leaks and spills. This liquor and the scrubber water may be recycled or discharged, generally with neutralization and sedimentation as the only treatment. Barometric condenser water is a major source of process wastewater at one plant. Table 15-3(a) shows the derivation of the model plant for the sodium chlorate subcategory.

DESCRIPTION OF PLANTS VISITED AND SAMPLED

Six of the 13 plants which produce sodium chlorate were visited during the study program. Of these, four plants were sampled for toxic and conventional pollutants. All four sampled plants (F122, F149, F146 and F112) produce sodium chlorate ($NaClO_3$) by the electrolysis of brine similar to the process shown in Figure 15-1.

Plants Sampled

At Plant F122, rock salt is dissolved in recycled water from the barometric condenser and river water to make up the brine for the process. The brine is purified to remove calcium carbonate and calcium sulfate, passed through a sand filter and then further treated to inhibit corrosion. The feed solution then undergoes chlorination and electrolysis at the cells and the cell liquor is

TABLE 15-3. WASTEWATER FLOW AT SODIUM CHLORATE FACILITIES(1)

Wastewater Source	Flow (m^3/kkg of Sodium Chlorate)								
	Plant Designation								
	F149	F147	F141	F146	F114	F131	F111	F136	F122
Direct Process Contact	0	4.12	0	0.001(3)	NA(4)	0	1.48	0	0
Indirect Process Contact	0.01	NA(2)	0	2.30	3.31(5)	0	23.2	1.52	NA(4)
Maintenance	0.07	NA(2)	0	0.53(4)	NA(4)	0	7.83	0.08(4)	NA(4)
Air Pollution Scrubbers	0.05	0.41	0	0.07(4)	NA(4)	0	NA(4)	0	NA(4)
TOTAL PROCESS WASTEWATER DISCHARGED	0.13	4.53	0	2.30	3.31	0	32.5	1.52	0
Noncontact Cooling	0	4.50	203	4.45	0.55	3.66(4)	68.6	182	0.32
Noncontact Ancillary	0	16.5	0	0.78	0	0	1.86	0	0
Storm Water	0.21	NA	NA	1.12	0	NA	NA	NA	0

NA Flow volume not available.
--- No information.

(1) Values indicated only for those plants that reported separate and complete information.
(2) Included in direct process contact water.
(3) Discharged at a solid waste to secure landfill. All other direct process contact wastewater is consumed or recycled.
(4) Wastewater recycled within plant.
(5) In January 1981, no indirect process contact water was discharged, however a hydrogen compressor was being installed and anticipated to generate wastewater.

Source: Section 308 Questionnaires and Plant Visit Reports

Table 15-3a

Sodium Chlorate Model Plant

Plant	Production (kkg/yr)	Total Plant Wastewater Excluding Contact Cooling Water and Including Condensate (m^3/day)	Approximate Unit Volume of Contact Cooling Water (m^3/kkg)	Approximate Unit Volume of Condensate (m^3/kkg)	Total Plant Wastewater Excluding Contact Cooling Water and Including Condensate (m^3/kkg)
F147	33,566	416.6	0	1.2	4.53
F146	40,823	257.2	0	-	2.3
F136	9,072	39.8	0	-	1.6
F149	18,144	6.5	0	-	0.13
F103	54,000	180.5	43	1.2	1.22 (e)
F122	46.800	147.5	61.8	1.15	1.15 (e)
F111	21,228	611.3	22	1.2	10.15 (e)
7 plants	223,633	1659.4			

Sodium Chlorate Model Plant

$$\text{Production} = \frac{\text{Total Production}}{\text{Number of Plants}} = \frac{23,633 \text{ kkg/yr}}{7} = 31,947.6 \text{ kkg/yr} = 32,000 \text{ kkg/yr}$$

$$\text{Unit Flow} = \frac{\text{Total Annual Discharge Flow}}{\text{Total Annual Production}} = \frac{1659.4 \text{ m}^3}{\text{day}} \times \frac{365 \text{ day}}{\text{yr}} \times \frac{\text{yr}}{223,633 \text{ kkg}} = 2.7 \text{ m}^3\text{/kkg}$$

$$\text{Daily Flow} = \frac{2.7 \text{ m}^3}{\text{kkg}} \times \frac{32,000 \text{ kkg}}{\text{yr}} \times \frac{\text{yr}}{365 \text{ day}} = 237 \text{ m}^3\text{/day} \quad (62,540 \text{ gpd})$$

(e) = estimate based upon process chemistry and subcategory plant performance evaporated to produce sodium chlorate crystals. Almost all product is sold as solid sodium chlorate.

River water is also used as make-up for the cooling water. Blowdown from the cooling tower collects in the cooling water supply sump and is discharged. The cooling water is treated with a corrosion inhibitor. All of the barometric condensate in the process area is recycled to the salt dissolving pit. Contact wastewater from spills, washdown, roof and floor drains is collected in the sumps. Part of this sump liquor is recycled and the rest is discharged. Wastewater from the chlorate process in excess of that recycled is discharged to an on-site lagoon. Effluents from other product processes also flow into the lagoon from where they are discharged to surface water. Figure 15-2 presents the sodium chlorate process and sampling points at Plant F122.

Sodium chloride from another on-site process is used in preparing the brine solution used in Plant 149. The brine is first prepared and treated, then is fed to the electrolytic cells, after which the solution undergoes treatment and filtration. The liquid product is partly marketed and partly used captively. Brine purification wastes are attributed to the other on-site process, hence, no brine purification wastes are assigned to the sodium chlorate process at this plant.

Sources of process wastewater include brine and caustic discharged by the air scrubbers, equipment leaks and spills, pump seal leaks, and equipment washdown. Equipment washdown includes general area washdown plus scheduled maintenance of the chlorate electrolytic cells and cleaning of the product filter. The process wastewater consists of the equipment washdown and maintenance wastewater plus the small portion of the scrubber wastewater and product filter backwash that cannot be recycled. All process wastewater is combined with other inorganic industrial wastewater sources, and undergoes equalization, neutralization and sedimentation before being discharged to a river. The process steps and wastewater sampling points at Plant F149 are shown in Figure 15-3.

Plant F146 uses purified brine obtained from another on-site operation. The brine undergoes further treatment and filtration to remove impurities. Chlorine is added to the brine prior to electrolysis for pH control in the cell. Sodium dichromate is also added to the brine. The cell liquor produced during electrolysis is resaturated with sodium chloride, treated with urea to remove hypochlorites, and filtered to produce a sodium chlorate solution.

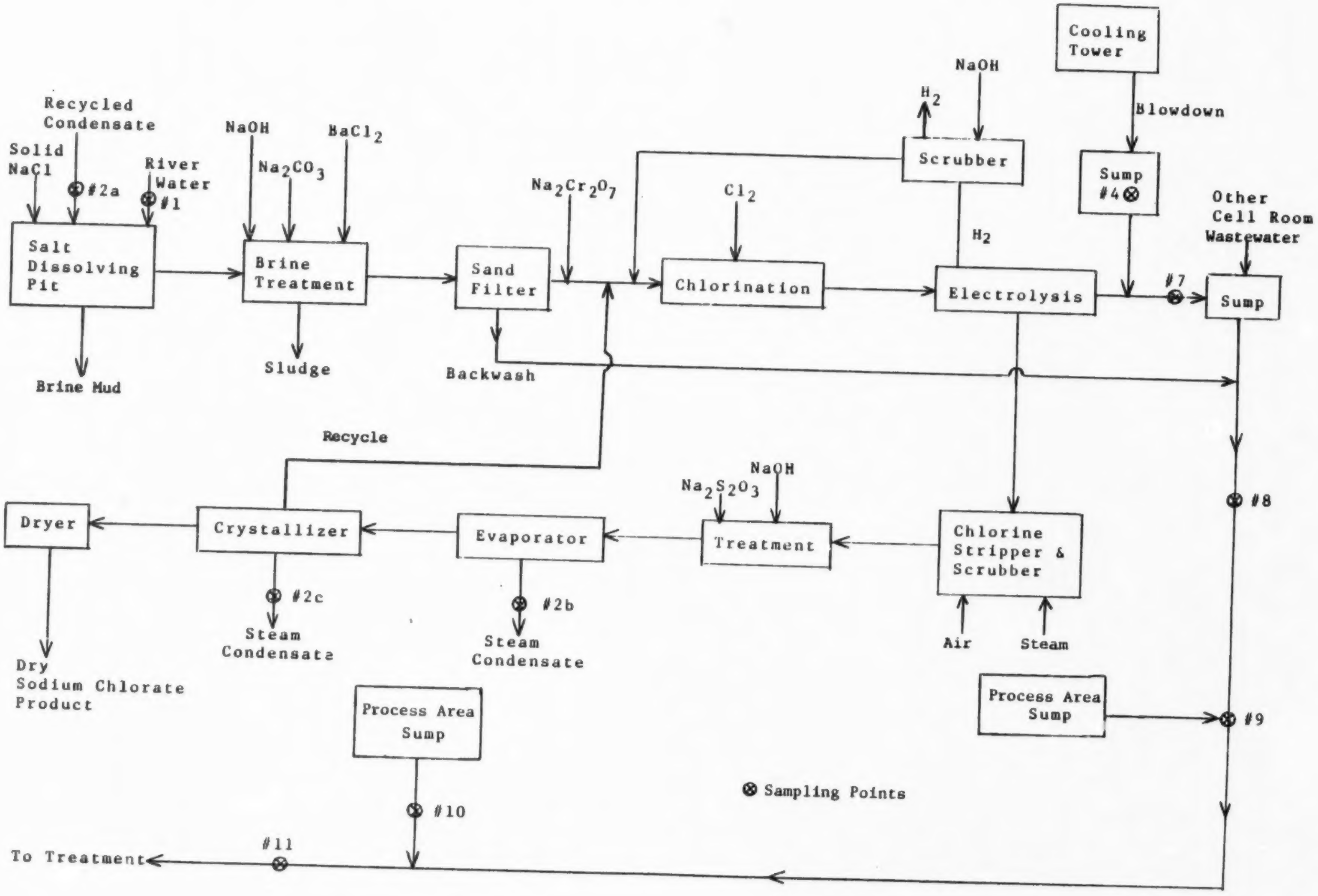

Solid NaCl
Recycled Condensate
#2a
River Water
#1
Salt Dissolving Pit
Brine Mud
NaOH
Na_2CO_3
$BaCl_2$
Brine Treatment
Sludge
Sand Filter
Backwash
$Na_2Cr_2O_7$
Cl_2
Chlorination
H_2
NaOH
Scrubber
H_2
Electrolysis
Cooling Tower
Blowdown
Sump #4
#7
Other Cell Room Wastewater
Sump
#8
Recycle
Dryer
Crystallizer
Evaporator
$Na_2S_2O_3$
NaOH
Treatment
Chlorine Stripper & Scrubber
Air
Steam
#2c
Steam Condensate
#2b
Steam Condensate
Dry Sodium Chlorate Product
Process Area Sump
#9
Process Area Sump
#10
Sampling Points
To Treatment
#11

FIGURE 15-2. PROCESS AND SAMPLING LOCATIONS FOR PLANT F122

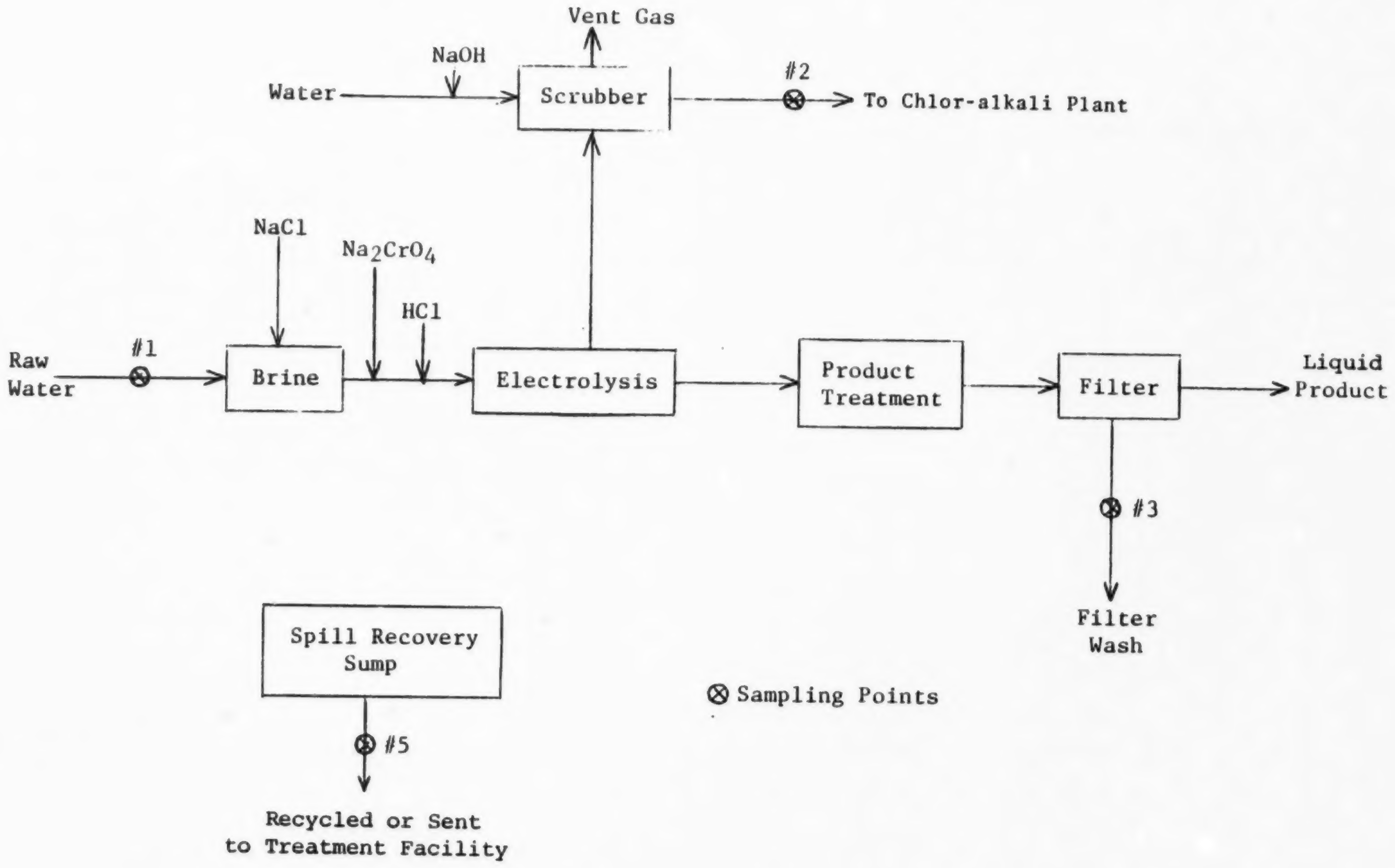

Vent Gas
NaOH
Water
Scrubber
#2
To Chlor-alkali Plant
NaCl
Na_2CrO_4
HCl
Raw Water
#1
Brine
Electrolysis
Product Treatment
Filter
Liquid Product
#3
Filter Wash
Spill Recovery Sump
#5
Recycled or Sent to Treatment Facility
⊗ Sampling Points

FIGURE 15-3. PROCESS AND SAMPLING LOCATIONS FOR PLANT F149

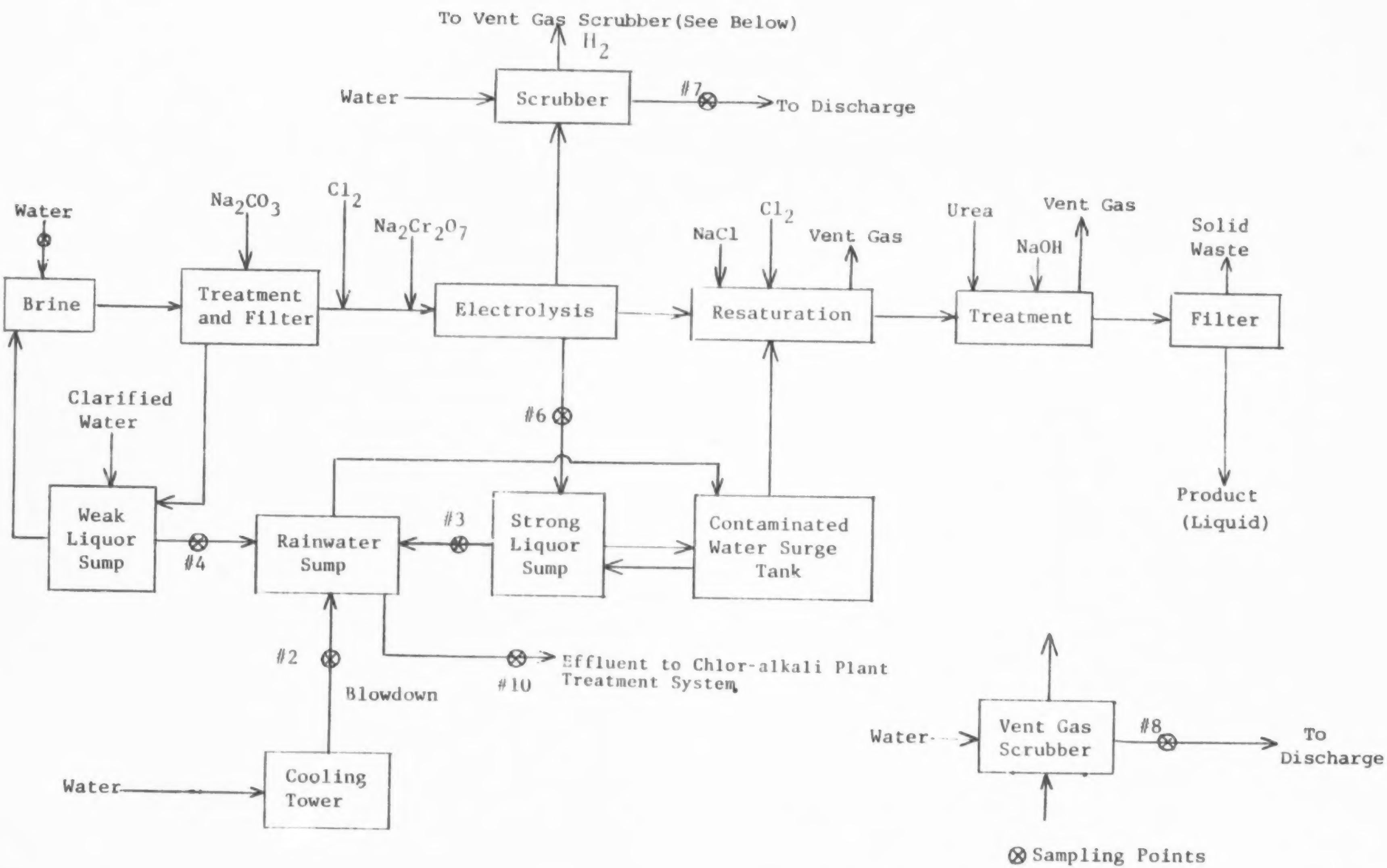

To Vent Gas Scrubber (See Below)
H_2
Water
Scrubber
#7
To Discharge
Water
Brine
Na_2CO_3
Treatment and Filter
Cl_2
$Na_2Cr_2O_7$
Electrolysis
NaCl
Cl_2
Vent Gas
Resaturation
Urea
NaOH
Vent Gas
Treatment
Solid Waste
Filter
Product (Liquid)
Clarified Water
#6
Weak Liquor Sump
#4
Rainwater Sump
#3
Strong Liquor Sump
Contaminated Water Surge Tank
#2
Blowdown
#10
Effluent to Chlor-alkali Plant Treatment System
Water
Cooling Tower
Water
Vent Gas Scrubber
#8
To Discharge
⊗ Sampling Points

FIGURE 15-4. PROCESS AND SAMPLING LOCATIONS FOR PLANT F146

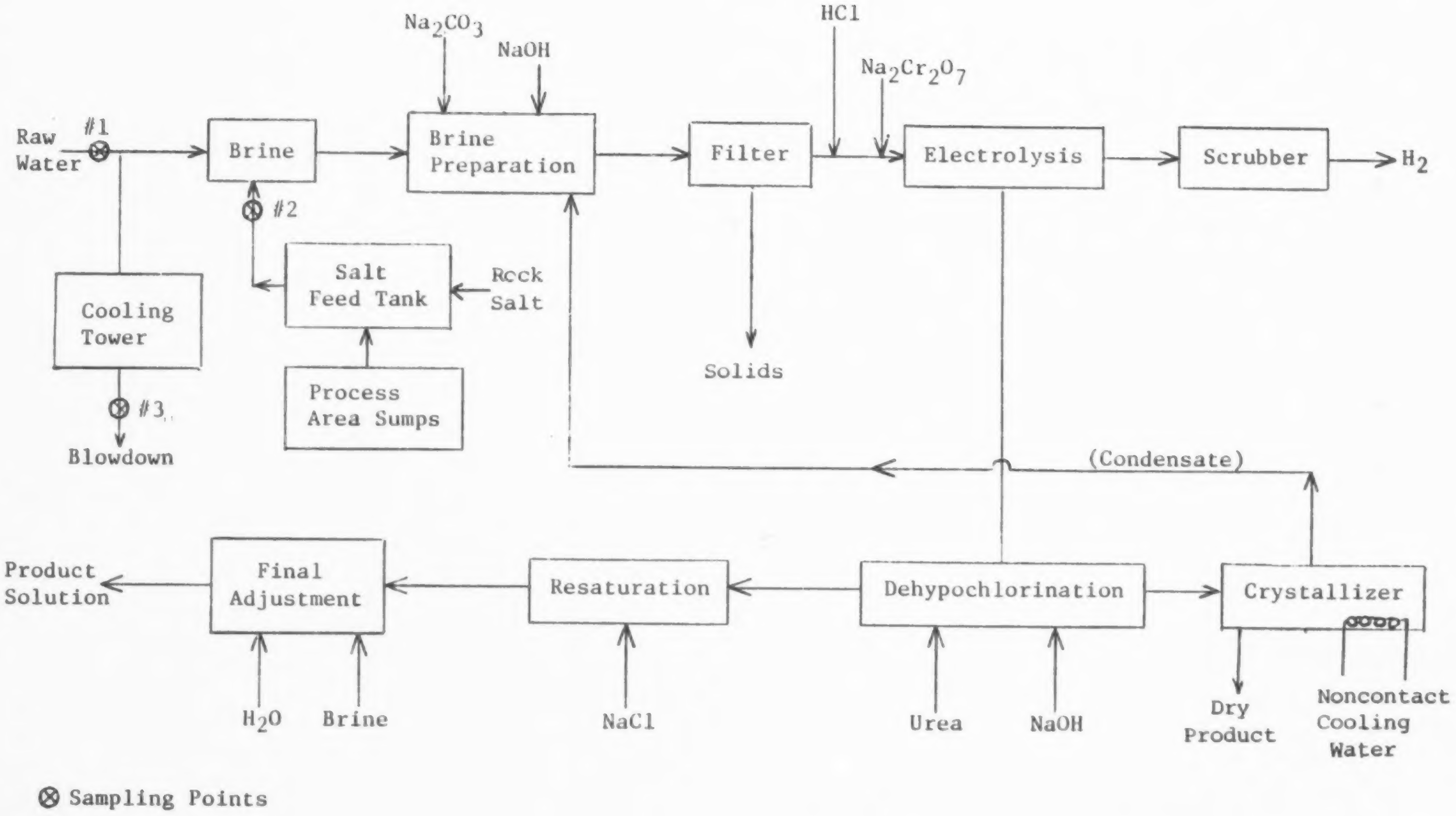

Raw Water
#1
Brine
#2
Cooling Tower
#3
Blowdown
Salt Feed Tank
Rock Salt
Process Area Sumps
Na$_2$CO$_3$
NaOH
Brine Preparation
Filter
Solids
HCl
Na$_2$Cr$_2$O$_7$
Electrolysis
Scrubber
H$_2$
(Condensate)
Product Solution
Final Adjustment
H$_2$O
Brine
Resaturation
NaCl
Dehypochlorination
Urea
NaOH
Crystallizer
Dry Product
Noncontact Cooling Water
⊗ Sampling Points

FIGURE 15-5. PROCESS AND SAMPLING LOCATIONS FOR PLANT F112

The contact wastewater sources consist of a strong and weak liquor. The strong liquor results from drainage from the cell pad sump and is recycled internally to the brine purification resaturator. The weak liquor consists of overflow from the brine purification filter, and drainage from the overflow filtrate receiver and clarified water, and is recycled to the brine pond. Hence, most brine purification wastes are attributed to the other on-site process, and little to sodium chlorate production at this plant. Noncontact cooling water (treated for corrosion and pH control) is recycled to a cooling tower, and tower blowdown may be discharged either manually or automatically to a rainwater sump. Plant effluent consists primarily of pump seal and tank seal water but also contains the overflow from the strong and weak liquor sumps, rainwater and blowdown from the cooling tower. The effluent is discharged to another plant downstream from the chlorate process and undergoes neutralization and sedimentation before discharge into the river. Figure 15-4 presents the wastewater sampling points and process steps at Plant F146.

Plant F112 obtains salt from an off-site source. A brine is produced, treated with sodium carbonate and caustic, and filtered before being fed to the electrolytic cells. The solution then undergoes dehypochlorination and resaturation. The product solution also undergoes final adjustment with water and brine before being marketed either as solid sodium chlorate or as a sodium chlorate solution. The filter residue from brine purification is dried to 80-90 percent solids and disposed as solid waste. There is no wastewater from the brine purification process at this plant. The plant does not filter the product solution and has no product filter backwash water.

Noncontact cooling water blowdown is the only wastewater stream generated at the facility and is discharged to a river. The cooling water is treated for corrosion control and also undergoes chlorination with Cl_2 gas and pH adjustment with H_2SO_4 before final discharge. All water from the process area sumps is recycled to the salt feed tanks. Figure 15-5 shows the process steps and sampling points at Plant F112.

Table 15-4 shows the wastewater stream flow and pollutant concentrations for the four sampled plants.

Other Plants Visited

The production of sodium chlorate at Plant F103 begins with the dissolution of rock salt in water and treatment of the resulting brine to remove impurities. The solution is adjusted for pH and electrolyzed. Caustic and urea are then added to reduce hypochlorite concentrations, the pH is adjusted and the liquor

TABLE 15-4. POLLUTANT CONCENTRATIONS AND LOADS FOR SAMPLED SODIUM CHLORATE FACILITIES(1)

Stream No.	Stream Description	TSS	Cr	Sb	Cl Residual(2)
		mg/l kg/kkg			
		Plant F122			
2A	Barometric condensate	<0.6 ---	0.22 ---	<0.007 ---	<0.5(4) ---
2B	Evaporator	3.7 ---	0.413 ---	<0.01 ---	<0.5(4) ---
2C	Crystallizer	6.0 ---	<0.014 ---	<0.007 ---	<0.5(4) ---
4	Cooling Water Blowdown	3.7 ---	3.10 ---	<0.15 ---	<0.5(5) ---
7	Cell Room Effluent(6)	2.0 ---	2.40 ---	<0.005 ---	1.4(7) ---
8	Cell Room Effluent	60.3 ---	1.00 ---	0.757 ---	81.3(7) ---
9	Process Area Effluent	5.3 0.698	0.68 0.0895	0.68 0.0895	44.3(7) 5.83
10	Process Area Effluent	290.0 38.2	36.67 4.83	0.024 0.00316	<185.6(7) <24.4
11	Final Effluent	12.3 3.24	1.30 0.342	0.46 0.121	18.2(7) 4.79
		Plant F149			
2	Scrubber Discharge	28.2 ---	0.52 ---	8.067 ---	ND
3	Filter Bag Wash	285.3 0.00524	24.33 0.00045	1.237 0.00002	ND
5	Spill Recovery Sump	75.8 0.0203	17.00 0.00455	1.933 0.00052	ND

Table 15-4. (continued)

Stream No.	Stream Description	TSS	Cr	Sb	Cl Residual(2)
		mg/l kg/kkg			
		Plant F146			
2	Noncontact Cooling Water	12.4 ---	0.058 ---	<0.013 ---	Detected ---
3	Strong Liquor Sump	112.9 ---	27.133 ---	3.737 ---	ND
4	Weak Liquor Sump(3)	213.5 ---	0.116 ---	<3.150 ---	ND
6	Cell Pad Sump(3)	299.5 ---	500.00 ---	4.050 ---	ND
7	Cell Gas Scrubber Wastewater	86.4 ---	0.330 ---	4.567 ---	ND
8	Vent Gas Scrubber Wastewater	148.0 ---	0.250 ---	2.933 ---	ND
10	Final Effluent	88.8 0.698	0.246 0.00193	<0.106 <0.00083	ND
		Plant F112			
2	Salt Feed Tank	100.7 ---	187.3 ---	9.13 ---	Detected ---
3	Cooling Tower Blowdown	6.0 0.0152	0.239 0.0006	0.333 0.00084	ND

--- Insufficient Information ND Not Detected

1. Flow and concentration values are average values for three days, except where noted.
2. Field tests were conducted for the presence of chlorine at all facilities sampled except at F122 where laboratory analyses were also performed.
3. Two-day sampling.
4. Laboratory testing for total residual chlorine.
5. Laboratory testing indicated <0.5 mg/l total residual chlorine, however field testing indicated the presence of chlorine.
6. One-day sampling.
7. Field testing indicated chlorine not detected.

filtered. The filtrate is evaporated and the hot solution is filtered and cooled to precipitate sodium chlorate crystals which are recovered by centrifuge.

Wastewater discharge consists primarily of noncontact cooling water which is not treated prior to discharge. Process wastewater from the spray condensers (less than four percent of total) may also be discharged; however, most of the condensate is recycled along with most other process contact wastewater as makeup water in the salt dissolvers. The air scrubber discharge is not recycled to the process but is commingled with the noncontact cooling water. Some of the product filter backwash is recycled and some is discharged. Undissolved solids from the brine purification process are commingled with the noncontact cooling water and discharged.

Plant F147 combines rock salt with sodium chlorate mother liquor which is then purified and filtered. The filtrate is sent to the electrolytic cells. The electrolyzed brine is treated with urea and caustic, filtered and crystallized. The sodium chlorate crystals are dried, packaged and shipped.

As mentioned above, the mother liquor following crystallization is recycled to the beginning of the process. The remaining process wastewater, including filter cake from filters and air scrubber wastewater is treated along with wastewater from another inorganic chemical product. Pollutants in the wastewater from the other inorganic chemical product effect hexavalent chromium and total residual chlorine removal. Treatment consists of two stage neutralization followed by settling prior to discharge to surface water.

Summary of Toxic Pollutant Data

Ten toxic metals were found in significant concentrations in the raw wastewater streams at the four sampled plants. Chromium, antimony, copper and lead appeared in the highest concentrations. A number of metals (e.g. arsenic, silver, thallium) were found at very low concentrations in three of the four plants, with Plant F149 containing the maximum observed concentration for these and several of the other metals. Toxic organics were found at all sampled plants with the exception of Plant F112 (cooling water only). Chloroform was the only organic found in common at the three remaining plants. Maximum observed concentrations in total combined raw wastewater streams of the sampled plants are summarized below.

TABLE 15-5. TOXIC POLLUTANT RAW WASTEWATER DATA FOR SAMPLED SODIUM CHLORATE FACILITIES

	Average Daily Pollutant Concentrations and Loads				
			mg/l kg/kkg		
Pollutant	F149	F146	F122	F112(1)	Avg.(2)
Antimony	1.933 0.00052	<0.106 <0.00083	0.459 0.121	0.333 0.00084	<0.833 <0.0408
Arsenic	0.210 0.00006	<0.005 <0.00004	<0.0027 <0.00071	<0.004 <0.00001	<0.073 <0.00027
Cadmium	<0.010 <0.000003	<0.010 <0.00008	<0.0043 <0.00113	<0.023 <0.00006	<0.0081 <0.00040
Chromium	17.000 0.00455	0.246 0.00193	1.300 0.342	0.239 0.00060	6.182 0.116
Copper	1.227 0.00033	0.090 0.00071	0.021 0.00553	0.357 0.00090	0.446 0.00219
Lead	1.033 0.00028	0.022 0.00017	<0.0041 <0.00108	0.215 0.00054	<0.353 <0.00051
Mercury	0.0057 0.000002	<0.002 <0.00002	0.145 0.0382	<0.008 <0.00002	<0.051 <0.0127
Nickel	0.640 0.00017	0.039 0.00031	0.149 0.0392	<0.117 <0.00030	0.276 0.0132
Silver	0.357 0.0001	<0.001 <0.00001	0.013 0.00342	0.001 0.000003	<0.124 <0.00118
Thallium	0.577 0.00015	<0.068 <0.00053	<0.031 <0.00816	<0.150 <0.00038	<0.225 <0.00295
Zinc	0.540 0.00014	0.140 0.0011	0.012 0.00316	0.613 0.00155	0.231 0.00147

---

1. Cooling Tower Blowdown only.
2. Includes only those plants with process wastewater samples, does not include Plant F112.

Pollutant	Maximum Concentration Observed (ug/l)
Antimony	2,000
Arsenic	610
Chromium	20,000
Copper	2,300
Lead	1,300
Mercury	220
Nickel	690
Silver	500
Thallium	1,100
Zinc	1,100
Benzene	83
Chloroform	220
1,2-Dichloroethane	4,710
Dichlorobromoethane	95
Chlorodibromoethane	27
Carbon Tetrachloride	19
Methyl Chloride	183
Methylene Chloride	12
Trichlorofluoromethane	27

Section 5 of this report describes the sampling program methodology. In the sodium chlorate industry, twelve days of sampling were conducted. Twenty-one streams were sampled and analyzed. The evaluation of toxic metal pollutants was based on 778 analytical data points while toxic organics evaluation consisted of 2,280 analytical data points. Table 15-5 presents the toxic pollutant raw waste data as the average daily concentrations found in the combined raw wastewater at the individual plants. The overall averages for the various pollutants are also included.

POLLUTION ABATEMENT OPTIONS

Toxic Pollutants of Concern

Toxic metals found in high concentrations in the wastewaters during sampling include chromium, lead and antimony. Chromium results from the addition of sodium dichromate to inhibit corrosion and to reduce the formation of hypochlorite ion. Other metals detected in the wastewaters may be contained in the raw material feed (brines or rock salt) which, in some cases, may be obtained from other product process wastewater streams. These impurities may be released to sodium chlorate wastewater streams during purification processes. The extensive use of recycling in this industry tends to build up the concentration of toxic pollutants in the mother liquor and in purges, leaks and washdowns.

While nine toxic organics were found above 10 ug/l in the raw wastewater streams, only one pollutant, 1,2-Dichloroethane, was found at significantly higher concentrations. This pollutant was present in all wastewater streams sampled at one facility. Its source is considered to be the river water which is used to dissolve the feed salt. The 1,2-Dichloroethane concentration in the sampled river water was 13,700 ug/l as opposed to 4,710 ug/l found in the total raw waste of the plant. Since the 1,2-Dichloroethane was found at only one plant and is related to its presence in the intake water at that plant, the Agency is excluding that pollutant under Paragraph 8(a) (iii) of the Settlement Agreement.

During a visit to one sodium chlorate facility, plant personnel indicated that chlorinated organics are generated by the use of graphite anodes; however, they also indicated that they had no data to demonstrate which chlorinated organics are generated or the amount generated.

Existing Wastewater Control and Treatment Practices

Control and treatment technologies at the plants which were visited and sampled were discussed previously. Control and treatment practices at the remaining sodium chlorate plants (F141, F114, F131, F111, F136, F105 and F135) are discussed briefly below.

Plant F141 does not discharge any process wastewater. Two lined evaporation ponds allow for solar evaporation and total recycle of the process wastewater streams. The plant is located in an arid region of the country. Approximately 15,000 m^3/day of noncontact cooling water is discharged to surface water during the summer months only. The plant uses pure salt as the raw material and has minimal brine purification wastewater. The product is sold as solid sodium chlorate.

Process wastewater streams in Plant F114 are recycled and blended with a brine solution obtained from an adjacent plant. In 1980, the plant was in the process of installing a liquid ring hydrogen compressor which would allow reuse of the gas as a boiler fuel. Seal water from the installed compressor would be the only process wastewater discharged from the plant. Brine purification wastes are attributed to the adjacent plant which provides the purified brine. The product is sold as the solution only.

Plant F131 does not discharge any wastewater streams to either surface waters or treatment facilities. Noncontact cooling water is discharged to an in-plant holding pond for use in dust control. The plant uses a pure salt as the raw material, with minimal brine purification wastes. The plant does not have air scrubbers, and produces only solution grade sodium chlorate. The product is not filtered before shipment.

Plant F111 discharges all wastewater streams to surface water. The largest source of wastewater flow is noncontact cooling water. Sources of process contact wastewater include brine purification and product filter backwashes, chlorate trench and cell flush streams, barometric condensate, and water used to purify hydrogen from cell off-gases. No information on any wastewater treatment, including in-plant treatment, is available but limited effluent data indicate that chlorine and chromium levels in the discharge are low. The plant uses an impure brine as raw material. Most of the product is sold as solid sodium chlorate.

At Plant F136, the source of raw material is purified brine from an adjacent chlor-alkali plant. Most wastewater is recycled, but excess air scrubber wastewater, washwater (cell wash and tank car wash) and pump seal water is combined with chlor-alkali wastewater and noncontact cooling water before pH adjustment and discharge.

At Plant F105, wastewater streams consisting of equipment wash water and cooling water are combined with pulp mill wastewater, clarified and aerated. The final effluent is discharged directly to surface water.

Plant F135 combines wastewater streams from sodium chlorate production with pulp mill effluent. No information is available on wastewater treatment technologies at this plant. The final effluent is discharged to surface water.

Other Applicable Control/Treatment Technologies

The existing treatment technology in the sodium chlorate industry consists of pH adjustment and sedimentation as the result of combination with wastewater streams from other products. Many facilities combine process wastewater with large volumes of noncontact cooling water for discharge. Of the plants which do discharge, only one case is known where treatment effects the removal of toxic metals and chlorine. Over half of the plants in the industry also practice either complete or extensive recycling of process wastewater. Other identified control or treatment technologies which might be applicable include hexavalent chromium reduction, dual-media filtration, and chlorine reduction.

The Zero Discharge Option

The amount of process wastewater that can be recycled and reused in the process depends critically on the source of the raw material (whether natural brines, purified brines, rock salt, or purified salt) and on the type of product sold (whether solid sodium chlorate or in water solution). Plants using rock salt or purified salt can recycle much of the process water, including barometric condenser water, to dissolve the salt; plants using brines cannot recycle much water for this purpose. Plants using purified brine or purified salt generate minimal amounts of brine purification process wastewater whereas plants using natural brines or rock salt must purify the brine before electrolysis, thus generating a significant amount of wastewater. Plants that produce a considerable portion of product as the water solution eliminate a significant amount of water that would otherwise be process wastewater with the product shipped. All four existing plants that have achieved zero discharge use a purified salt as raw material and three of the four ship a considerable portion of the product in solution (the one plant of these four that ships primarily solid sodium chlorate is located in an arid region of the country and recycles process water through an evaporation pond).

One other zero discharge plant is also located in an arid region. A third plant uses a very pure salt from an adjacent plant and generates no brine purification wastewater, which allows complete recycle of the remaining process wastewater. The fourth plant evaporates the water from the residue from brine purification (there is little water generated from purification of the brine from a purified salt anyhow), and does not filter its product solution, thus eliminating that source of wastewater also. The customers for the fourth plant apparently do not require filtration of the product solution. Since the four plants achieve zero discharge through special circumstances (access to an economic source of purified salt, customer preference for solution grade product, and/or location in an arid region of the country), the zero discharge option is not technically feasible for the average plant.

Process Modifications and Technology Transfer Options

Process modifications which have been implemented at sodium chlorate plants which reduce the amount of process wastewater discharged include the following:

1. Recycle of scrubber wastewater within the scrubber to improve reagent utilization.

2. Use of sodium hydroxide as the alkali in the scrubbers so that the water is amenable to reuse in the plant. Calcium-based alkalies reduce the efficiency of electrodes by forming a coating on the electrode

3. Use of noncontact evaporators and crystallizers in the production of solid sodium chlorate. Noncontact water would thus be used which would reduce the amount of process contact water. Plants practicing contact cooling through the use of barometric condensers generate large amounts of slightly contaminated wastewater. Two plants use the contact cooling water to dissolve the raw salt to make the brine.

4. Operations using rock salt use the recycled wastewater in dissolving the salt.

5. Use of a coated titanium anode instead of a graphite electrode. Graphite electrodes may contain lead dioxide and are also consumed more rapidly in the process. The elimination of a source of lead, reduced generation of solid waste (graphite), and elimination of a source of chlorinated organics can be obtained using coated titanium anodes. However, the primary reason many manufacturers are switching to coated titanium anodes is increased electrical efficiency.

No other process modifications or technology options which would reduce the amount of wastewater discharged were identified.

Best Management Practices

Recycle of some wastewater streams is already extensively practiced in this industry. Collection and recycle of pump seal water and spills is employed at several facilities. Rain water, to the extent possible, should be diverted around salt storage pads and other contact areas. The use of high purity brine or salt can minimize pretreatment of the salt and generation of wastewater; however, the purity of the salt used is usually an economic decision. In combination with recycle the use of high purity salt may enable the attainment of zero discharge.

The use of chromate and its concentration in the cell should be reduced to the lowest concentration feasible for cell use to reduce the cost of production and reduce the cost of wastewater treatment.

Advanced Treatment Technology

In some case, additional treatment may be required to reduce chromium and antimony to lower concentrations. Level 2 treatment technology may be needed to accomplish adequate removal.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1

Level 1 treatment consists of hexavalent chromium and chlorine reduction, alkaline precipitation, settling, pH adjustment and sludge dewatering. This technology is illustrated in Figure 10-16. A holding basin for equalization sized to retain 4-6 hours of flow is provided.

The pH of wastewater leaving the holding basin must be reduced by the addition of concentrated sulfuric acid to a pH range of 2 to 3. This pH is necessary to reduce hexavalent chromium to trivalent chromium. A reducing agent such as sodium bisulfite is then added to the wastewater (sulfur dioxide, sodium metabisulfite, or ferrous iron are alternative reagents which could also be used to reduce hexavalent chromium). Hydrated lime is then added to the wastewater to elevate the pH to approximately 8.5 to produce a chromium (trivalent) hydroxide precipitate. The chromium hydroxide and other solids are allowed to settle in a clarifier. The overflow from the clarifier is aerated and neutralized (if necessary) before discharge. A monitoring system is installed at the discharge point. The reducing agent, sodium bisulfite, is also effective as a means of total residual chlorine reduction.

Sludge collected in the clarifier is directed to a filter press for dewatering. Pits are provided at the filter press for the temporary storage of sludge. The sludge is periodically transported off-site to a hazardous material landfill. The objective of Level 1 is to reduce the chlorine residual and to reduce hexavalent chromium to trivalent chromium, and then to precipitate chromium, antimony, other heavy metals and suspended solids.

Level 1 treatment was selected as the basis of BPT because it represents a viable industry practice for the control of hexavalent and total chromium, antimony, total residual chlorine, and suspended solids. No other technologies will obtain significant removals of these pollutants. Currently, one of nine direct dischargers in the sodium chlorate industry has the technology or its equivalent installed. Four facilities achieve zero discharge and thus would not be affected. In addition, two of the direct dischargers direct their wastewater to a paper or pulp mill for use or treatment. The effluent reduction to be achieved by Level 1 technology justifies the cost involved.

B. Level 2

Level 2 treatment consists of granular media filtration for the additional removal of suspended solids containing precipitated chromium hydroxide and antimony from the effluent. Sludges from brine purification and chromium hydroxide precipitates would be removed by filtration. Dual-media filtration is preferred because it overcomes the limitations on loadings normally encountered with sand filters due to the high flow rates encountered in this subcategory. Level 2 was selected as BAT because it provides significant additional removal of antimony and chromium.

Equipment for Different Treatment Levels

A. Equipment functions

A conventional type clarifier is used to remove the suspended solids. A plate and frame filter press is used for sludge dewatering and the filtrate from the filter is returned to the lime mixing tank. Level 2 requires the addition of a granular media filter, typically anthracite and sand, to handle a higher loading. All equipment is conventional and readily available.

B. Chemical Handling

Concentrated sulfuric acid is added to lower the pH using conventional acid handling equipment. Sodium bisulfite is manually added to a chemical feed system which is fed into a mixing reaction tank. A conventional hydrated lime storage and feed system is used to proportionally add the proper amount of lime.

C. Solids Handling

Treatment sludges produced by Levels 1 and 2 are directed to a sludge holding basin from which it is fed to the filter press. The solids produced by the filter are assumed to be dewatered to 50 percent solids by volume and disposed of in an off-site hazardous materials landfill. The sludge was assumed to be hazardous because of its high metal content.

Treatment Cost Estimates

In the sodium chlorate industry, costs were developed for one model plant representing the average production and flow. The Agency in developing the proposed regulations considered data from all plants in the subcategory. The Agency used flow data from the seven dischargers which provided sufficient flow data in developing the model plant unit flow (See Table 15-3(a). (Two dischargers did not provide flow data; those plants are pulp and paper mills using the typical production process and would be expected to produce solution grade product for internal use. Therefore, the flow from those two plants is believed to be within the range of flows observed at other plants). The unit flow does not include barometric condenser wastewater because one of the three plants using barometric condensers completely recycles the barometric condenser wastewater and a second recycles most of it. The barometric condenser wastewater is considered process wastewater, and the proposed limitations would include pollutants discharged with the barometric condenser wastewater. The barometric condenser wastewater is high in volume but low in pollutant concentrations, and those plants where the barometric condenser wastewater is discharged separately from the rest of the process wastewater should have no difficulty in achieving the proposed limitations since treatment of the low volume concentrated wastewaters should be sufficient. However, plants that mix barometric condenser wastewater with other process wastewater before discharge will be at a distinct disadvantage because the resulting wastestream will be high in volume (thus increasing treatment plant size and costs) and lower in concentration of pollutants (thus reducing the efficiency of the treatment). In developing the proposed limitations and model plant, the Agency assumed that plants that mixed barometric condenser wastewater with other process wastewater could economically separate the other process wastewater from the barometric condenser wastewater for treatment. However, since the costs for such a separation are highly site specific, the Agency has been unable to quantify those costs, and they are not included in the treatment system costs. At proposal, we requested comment and data on this issue. However, no comments or data were provided. Therefore, the Agency concludes that separation of barometric condenser water from other process wastewater can be economically accomplished. Therefore, the Agency is promulgating the regulations as proposed.

General

Production ranges and wastewater flow characteristics have been presented earlier in this section and are summarized in Table 15-1. There are nine direct dischargers and four plants which achieve zero discharge. No plants in this subcategory discharge to a POTW.

A. Sodium Chlorate

The model plant for the sodium chlorate subcategory has a production rate of 32,000 metric tons per year and a daily flow rate of 237 cubic meters per day. These figures were used as the basis for the treatment cost estimates at both levels. See Figure 15-3(a).

Material usage for both levels is estimated as follows:

Chemical	Amount	Treatment Level
H_2SO_4 (100 percent)	59.25 kg/day	1
NaOH (50 percent sol.)	152.6 kg/day	1
Sodium Bisulfite	33.2 kg/day	1

Total solid waste generated is estimated at 0.021 m^3/day for Level 1 and an additional 0.002 m^3/day for Level 2.

Model Plant Treatment Costs. On the basis of the model plant specifications and design concepts presented earlier and in Section 10, the estimated costs of treatment for one model with two levels are shown in Table 15-6. The cost of Level 2 is incremental to Level 1.

Basis for Regulations

Basis for BPT Limitations

A. Technology Basis

For BPT, the Agency is setting limitations based upon hexavalent chromium reduction, chlorine destruction, alkaline precipitation, clarification, final pH adjustment (if necessary) and sludge dewatering (Level 1). Of the nine direct dischargers in this subcategory, one facility has BPT or its equivalent installed. One additional facility may achieve the BPT levels based on limited effluent data. Two direct dischargers discharge their effluent to a paper or pulp mill. The majority of direct dischargers currently provide less than Level 1 treatment of process wastewater. Four additional plants achieve zero discharge and thus would not be affected.

TABLE 15-6. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Sodium Chlorate

ANNUAL PRODUCTION: 32,000 METRIC TONS

DAILY FLOW: 237 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2
Facilities	21.2	
Installed Equipment (Including Instrumentation)	191.1	27.4
Engineering	42.5	5.5
Contractor Overhead and Profit	38.2	4.9
Contingency	29.3	3.8
Land		
Total Invested Capital	322.3	41.6
Annual Capital Recovery	52.4	6.8
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	109.0	9.8
Residual Waste Disposal	0.4	Negl.
Total Annual Cost	161.8	16.6

b. TREATMENT DESCRIPTION

LEVEL 1: Hexavalent chromium reduction, chlorine reduction, alkaline precipitation, clarification, sludge dewatering, pH adjustment

LEVEL 2: Filtration

B. Flow Basis

For the sodium chlorate subcategory, a unit flow rate of 2.7 m^3/kkg was selected as being representative of the group. This flow was derived as shown on Table 15-3(a). Accordingly, the model plant has a daily flow of 237 cubic meters, based on production of 32,000 kkg per year and 365 operating days per year.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are being established is based on an evaluation of the raw wastewater data from screening and verification, consideration of the raw materials used in the process, literature data, historical discharge monitoring reports and permit applications, and the treatability of the toxic pollutants.

Tables 8-1 through 8-14 summarize the achievable concentrations of toxic metal pollutants from the literature using available technology options, other industries, and treatability studies. Water use and discharge data are presented earlier in Section 15 together with generalized process characteristics. Pollutant concentrations of raw wastewater streams and a summary of maximum concentrations observed of toxic pollutants detected during screening and verification sampling at several plants are also presented earlier in this section. Data from Appendix A on the performance of in-place industry treatment systems was also utilized in developing the list of pollutants to be regulated.

Based upon the occurrence of treatable levels of specific toxic metals, antimony and chromium were selected as candidate toxic pollutants for BPT regulation. Chromium is added to the process at sodium chlorate plants. Antimony was detected in cell room wastes and scrubber discharges at all four plants sampled. Copper, lead, thallium and zinc were detected but at less than treatable levels. Because the wastewater streams that contain hexavalent chromium also contain chlorine, and because both hexavalent chromium and chlorine will be reduced simultaneously by the sodium bisulfite, the Agency has also selected chlorine for regulation at the BPT level.

Consideration of the raw wastewater characteristics, widespread industry use, and information in Section 8 related to the effectiveness of hexavalent chromium and chlorine reduction, alkaline precipitation, and settling led to the selection of antimony and chromium as the toxic pollutants to be regulated.

D. Basis of BPT Pollutant Limitations

Limitations are presented as both concentrations (mg/l) and loads (kg/kkg), and the relationship between the two is based on a unit flow rate of 2.7 m^3/kkg.

BPT limitations, which apply to all process wastewater discharged, are presented in Table 15-8.

1. Conventional Pollutants

a. pH

The treated effluent is to be controlled within the range of 6.0 - 9.0. This limitation is based upon the data presented in Appendix B of the Development Document for Proposed Effluent Guidelines for Phase I Inorganic Chemicals (Ref. 3) and the JRB study (Ref. 4).

b. TSS

Three Phase II plants (F125, F115 and F140) considered to be efficiently operating their wastewater treatment facilities provided long-term Level 1 treatment system performance data for TSS. TSS data from Plant F144 were not used because the wastewater is passed through a limestone bed in the first stage of the plant's neutralization system. This would reduce the TSS loading to the clarifier giving lower TSS results than expected for the average inorganic chemicals plant. Since no other data from well-operated Level 1 treatment systems was available, and since the clarification provided at plants F125, F115 and F140 for TSS removal would be similar to that necessary for TSS removal at sodium chlorate plants, the BPT limitations for TSS are based upon a summary of long-term data from Plants F125, F115 and F140. The long-term average of 13 mg/l was used to develop discharge limitations. Variability factors of 1.9 for a monthly average and 3.3 for a 24 hour maximum were used yielding TSS concentration limits of 25 mg/l and 43 mg/l, respectively. The monthly average variability factor was obtained from the variability factors from all three plants with long-term data employing Level 1 type treatment. Since the data from all three plants was not in a form which could be used to develop daily maximum variability factors, the daily maximum variability factor of 3.0 for filters was adjusted upward by 10% to account for the higher variability experienced with clarification only. Thus, utilizing these values, one obtains TSS mass limitations for the sodium chlorate subcategory of:

30-day average:

$(25\ mg/l)(2.7\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.068\ kg/kkg$

24-hour maximum:

$(43\ mg/l)(2.7\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.12\ kg/kkg$

2. Toxic Pollutants

a. Chromium (Total)

Since there is no long-term performance data for this subcategory, the long-term average concentration for chromium is based on industrial wastewater system performance data found in Table 8-12 and the promulgated total chromium limitations for the sodium dichromate subcategory, which uses a similar wastewater treatment system for chromium control. The variability factor ratio is based on those used for the Sodium Dichromate subcategory. The long-term average used was 0.25 mg/l. Variability factors of 2.0 for the 30-day average and 4.0 for the 24-hour maximum from the Sodium Dichromate subcategory were used, yielding chromium limitations of 0.5 mg/l and 1.0 mg/l respectively. Thus utilizing these values, mass limitations for the sodium chlorate subcategory may be obtained as follows:

30-day average:

$(0.5\ mg/l)(2.7\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.0014\ kg/kkg$

24-hour maximum:

$(1.0\ mg/l)(2.7\ m^3/kkg)(kg/10^6\ mg)(1000\ l/m^3)$
$= 0.0027\ kg/kkg$

b. Antimony (total)

Since there is no long-term average performance data for this industry, the long-term average concentration for antimony is based on industrial wastewater treatment system performance data found in Table 8-11. The lowest reported achievable concentration for antimony with a lime precipitation and clarification system (0.8 mg/l) was used as the long term average. The variability factors of 2.0 for 30-day average and 4.0 for the 24-hour maximum used for chromium were used for antimony, yielding antimony effluent concentrations of 1.6 mg/l and 3.2 mg/l respectively. Utilizing these values, mass limitations for antimony are obtained as follows:

30-day average:

$(1.6 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6\text{mg})(1000 \text{ l/m}^3)$
$= 0.0043 \text{ kg/kkg}$

24-hour maximum:

$(3.2 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6\text{mg})(1000 \text{ l/m}^3)$
$= 0.0086 \text{ kg/kkg}$

3. Non-conventional Pollutants

a. Chlorine (Total Residual)

Since there is no long-term performance data for this industry, the BPT limitations for chlorine are based on the long-term monitoring data for chlorine in the chlor-alkali subcategory which uses a similar wastewater treatment technology for chlorine control. (See the Phase I Development Document, Appendix A, Plant A). The variability factors are based on that same facility. The plant is achieving a long-term average total residual chlorine concentration of 0.64 mg/l. The variability factors for this longterm average are 1.4 for the 30-day average and 2.3 for the 24-hour maximum. These variability factors yield effluent limitations of 0.9 mg/l and 1.5 mg/l, for the 30-day average and 24-hour maximum respectively. The mass limitations for chlorine in the sodium chlorate subcategory are as follows:

TABLE 15-7. BPT EFFLUENT LIMITATIONS FOR SODIUM CHLORATE

Conventional Pollutants	Long-Term Avg. (mg/l)	VFR	Conc. Basis (mg/l) 30-day avg.	Conc. Basis (mg/l) 24-hr. max.	Effluent Limit (kg/kkg) 30-day avg.	Effluent Limit (kg/kkg) 24-hr. max.
TSS	13 (1)	1.9/3.3 (1)	25	43	0.068	0.12
Toxic Pollutants						
Antimony (Total)	0.8*	2/4 (2)	1.6	3.2	0.0043	0.0086
Chromium (Total)	0.25 (2)	2/4 (2)	0.5	1.0	0.0014	0.0027
Non-Conventional Pollutants						
Chlorine (Total Residual)	0.64 (3)	1.4/2.3 (3)	0.9	1.5	0.0024	0.0041

LTA = Long-term average achievable level.

VFR - Variability Factor Ratio

(1) Based upon long-term data at Plants F115, F125 and F140.
(2) LTA used as basis for promulgated limitations for Sodium Dichromate Subcategory - Phase I.
(3) LTA and limitations based upon promulgated total residual chlorine limitations for Chlor-Alkali subcategory - Phase I - Chlor-Alkali Mercury Cell Subcategory.

*From Table 8-11.

See Phase I Inorganic Chemicals Development Document; EPA 440/1-82-007.

__30-day average__:

$(0.9 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.0024 \text{ kg/kkg}$

__24-hour maximum__:

$(1.5 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.0041 \text{ kg/kkg}$

Basis for BCT Effluent Limitations

On October 29, 1982, EPA proposed a new and revised methodology for determination of BCT for conventional pollutants. In this subcategory, only two conventional pollutants have been selected for limitation, pH and total suspended solids (TSS). Two tests are required according to the revised methodology, a POTW test and an industry cost-effectiveness test. Under the proposed methodology, the POTW test is passed if the incremental cost per pound of conventional pollutant removed in going from BPT to BCT is less than $0.46 per pound in 1981 dollars. The industry test is passed if the same incremental cost per pound is less than 143 percent of the incremental cost per pound associated with achieving BPT.

The methodology for the first BCT cost test is as follows:

(1) Calculate the amount of additional TSS removed by the BCT technology.

(a) BPT long-term average = 13 mg/l
Level 2 long-term average* = 9.3 mg/l
Difference 3.7 mg/l

*(See Sections 11 and 12 for derivation)

(b) Annual flow for model plant:
$(2.7 \text{ m}^3\text{/kkg})\ (32{,}000 \text{ kkg/yr}) = 86{,}400 \text{ m}^3\text{/yr}$

(c) Total annual additional TSS removed for model plants

$(3.7 \text{ mg/l})\ (86{,}400 \text{ m}^3\text{/yr})\ (\text{kg}/10^6\text{mg})(1000 \text{ l/m}^3)$
$= 320 \text{ kg/yr}$
$= 705 \text{ lbs/yr}$

(2) Calculate incremental cost, in dollars per pound of TSS removed, for the model plant.

(a) Incremental annualized cost of Level 2 technology, from Table 15-6: $16,660 per year.

(b) Divide annualized cost by annual TSS removal: ($16,600 per year) ÷ (705 Lbs per year) = $23.56 per pound of TSS removed.

This is far above the $0.46 per pound bench mark cost. Therefore, the candidate BCT technology failed the first BCT cost test and there is no need to apply the second BCT cost test.

On October 29, 1982, EPA proposed a revised BCT methodology. While EPA is considering revising that methodology, we have determined that in this subcategory no technology beyond BPT will pass the proposed BCT cost test or any other BCT test that the Agency is likely to adopt. Accordingly, in this subcategory we are setting BCT equal to BPT. As a result, BCT for TSS is equal to the BPT limitations. However, the Agency will need to reconsider the BCT limitations for this subcategory when a new BCT cost test is promulgated.

Basis for BAT Effluent Limitations

Application of Advanced Level Treatment

Utilizing the cost estimates in this report, the Agency has analyzed the cost of the base level system (BPT = Level 1) and the advanced level option for toxic pollutant removal. The economic impacts on the Sodium Chlorate Subcategory have been evaluated in detail and taken into consideration in the determination of the BAT regulations.

For BAT, the Agency is promulgating limitations based on treatment consisting of Level 1 plus Level 2. Level 2 adds granular media filtration of the Level 1 effluent. The toxic pollutants limited by the promulgated BAT regulation are antimony and chromium. The non-conventional pollutant to be regulated is total residual chlorine.

A. Technology Basis

The overflow from the clarifier is filtered in a granular media filter to remove additional antimony and chromium from the waste stream. The backwash from the filters is returned to the clarifier or if the solids concentration is sufficiently high the backwash is directed to the filter press for dewatering. The filter will not remove additional amounts of chlorine.

B. Flow Basis

A unit flow rate of 2.7 m^3/kkg of sodium chlorate wastewater has been selected for BAT (same as BPT).

C. Selection of Pollutants to be Regulated

Toxic Pollutants

Antimony and chromium have been selected as the toxic pollutants for control under BAT, as both pollutants have been detected at sodium chlorate plants at significant, treatable concentrations. Table 15-9 presents the BAT limitations for the Sodium Chlorate Subcategory.

a. Chromium

Since there is no long-term treatment system performance data for this industry, the estimated achievable long-term average concentration of 0.16 mg/l for chromium from Table 8-13 is used for the long-term average. The variability factors of 2.0 for the 30-day average and 4.0 for the 24-hour maximum used for chromium at the BPT level are used for BAT, yielding effluent concentrations of 0.32 mg/l and 0.64 mg/l, respectively. The mass limitations for chromium in the sodium chlorate subcategory are calculated as follows:

30-day average:

$(0.32 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.00086 \text{ kg/kkg}$

24-hour maximum:

$(0.64 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6)(1000 \text{ l/m}^3)$
$= 0.0017 \text{ kg/kkg}$

b. Antimony

Since there is no long-term treatment system performance data for this industry, the estimated achievable long-term average concentration is taken from industry performance data in Table 8-11. The lowest reported achievable concentration of 0.4 mg/l for antimony utilizing lime addition plus filtration is taken as the long-term average. The variability factors of 2.0 for 30-day average and 4.0 for 24-hour maximum used for chromium are used for antimony, yielding

TABLE 15-8. BAT EFFLUENT LIMITATIONS FOR SODIUM CHLORATE SUBCATEGORY

Toxic Pollutants	Long-Term Avg. (mg/l)	VFR	Conc. Basis (mg/l)		Effluent Limit (kg/kkg)	
			30-day avg.	24-hr. max.	30-day avg.	24-hr. max.
Antimony (T)	0.4*	2/4(2)	0.80	1.6	0.0022	0.0043
Chromium (T)	0.16(1)	2/4(2)	0.32	0.64	0.00086	0.0017
Non-Conventional Pollutants						
Chorine (Total Residual)	0.64(3)	1.4/2.3(3)	0.9	1.5	0.0024	0.0041

LTA = Long-term average achievable level.

VFR - Variability Factor Ratio; ratio of the 30-day average variability factor to the 24-hour maximum variability factor.

(1) From Table 8-13.
(2) Phase I Inorganic Chemicals Development Document; EPA 440/1-82/007, variability factors for Sodium Dichromate.
(3) See Table 15-7.

*From Table 8-11.

effluent antimony concentrations of 0.8 mg/l and 1.6 mg/l respectively. The mass limitations are calculated as follows:

30-day average:

$(0.80 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6)(1000 \text{ l/m}^3)$
$= 0.0022 \text{ kg/kkg}$

24-hour maximum:

$(1.6 \text{ mg/l})(2.7 \text{ m}^3\text{/kkg})(\text{kg}/10^6 \text{ mg})(1000 \text{ l/m}^3)$
$= 0.0043 \text{ kg/kkg}$

Non-Conventional Pollutants

Total residual chlorine has been selected for control under BAT but is not reduced by Level 2 technology. Therefore, the concentrations and loading promulgated for BAT are the same as for BPT for this parameter.

Basis for NSPS Effluent Limitations

For NSPS, the Agency is promulgating limitations based on the BAT technology since no technology which would remove significant additional amounts of pollutants is known. The pollutants limited include pH, TSS, antimony, chromium (total), and chlorine (total residual).

The limitations for antimony and chromium are the same as BAT. See pages 368 and 370 for the development of these limitations. The limitations for pH and total residual chloride are the same as for BPT. See pages 362 and 364 for the development of those limitations. The TSS limitations are based on filtration and are developed as follows:

> Since no long-term monitoring data for TSS is available from any sodium chlorate plant with Level 2 treatment, the NSPS limitations for TSS are based on an average of long-term TSS monitoring data from Plants A and K as presented in Appendix A of the Phase I Development Document which uses the same Level 2 (filtration) technology to control TSS that is promulgated for the sodium chlorate subcategory. A long-term average of 9.3 mg/l (the average of both plants) was used to develop the discharge limitations for plants employing filtration. Variability factors, also obtained from Plants A and K, of 1.8 for a monthly average and 3.0 for a 24-hour maximum were used yielding TSS concentration limits of 17 mg/l and 28 mg/l respectively.

TABLE 15-9. NSPS EFFLUENT LIMITATIONS FOR SODIUM CHLORATE

Conventional Pollutants	Long-Term Avg. (mg/l)	VFR	Conc. Basis (mg/l) 30-day avg.	Conc. Basis (mg/l) 24-hr. max.	Effluent Limit (kg/kkg) 30-day avg.	Effluent Limit (kg/kkg) 24-hr. max.
TSS	9.3(1)	1.8/3.0(1)	17	28	0.046	0.076
Toxic Pollutants						
Antimony(T)	0.4*	2/4(2)	0.80	1.6	0.0022	0.0043
Chromium(T)	0.16(3)	2/4(2)	0.32	0.64	0.00086	0.0017
Nonconventional Pollutants						
Chlorine (Total Residual)	0.64(4)	1.4/2.3(3)	0.9	1.5	0.0024	0.0041

LTA - Long-term average achievable level.

VFR - Variability Factor Ratio; ratio of the 30-day average variability factor to the 24-hour maximum variability factor.

(1) Based upon long-term data at Plants A and K (Phase I).
(2) Phase I Inorganic Chemicals Development Document; EPA 440/1-82/007, variability factors for Sodium Dichromate.
(3) FRom Table 8-13.
(4) See Table 15-7.
* From Table 8-11.

Thus, utilizing these values, one obtains TSS mass limitations for the sodium chlorate subcategory of:

30-day averages:

(17 mg/l)(2.7 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.046 kg/kkg

24-hour maximum:

(28 mg/l)(2.7 m^3/kkg)(kg/10^6 mg)(1000 l/m^3)
= 0.076 kg/kkg

The NSPS limitations are found in Table 15-9.

Basis for Pretreatment Standards

Pretreatment is necessary because it provides better removal of antimony and chromium than is achievable by a well operated POTW with secondary treatment installed, and thereby prevents pass-through that would occur in a POTW in the absence of pretreatment.

Using the summary data presented in Tables 15-5 and 15-8, the Agency has estimated the percent removals for antimony and chromium by comparing the treated waste concentration for the selected BAT technology for those two toxic metals with the average untreated waste concentrations for those same two pollutants. The calculation is as follows:

Antimony: Raw Waste = 0.83 mg/l
BAT = 0.4 mg/l

Percent Removal = [(0.833 - 0.4) ÷ (0.8)] (100)
= 52%

Chromium (Total): Raw Waste = 6.2 mg/l
BAT = 0.16 mg/l

Percent Removal = [(6.2 - 0.16)/(6.2)] (100)
= 97%

The percent removal for total chromium is greater than the removals achieved by 25% of the POTWs in the "50 Cities" study (Fate of Priority Pollutants in Publicly Owned Treatment Works, Final Report, EPA 440/1-82/303, September, 1982). There is limited data available on the removal of antimony by a POTW, but removals for other toxic metals range from 19% to 66% for 25% of the POTWs in that study. Therefore, the Agency believes it is prudent to assume that antimony could pass through a POTW. Since both chromium and antimony pass through a well operated POTW with secondary treatment, pretreatment is necessary.

Using the summary data presented in Tables 15-5 and 15-7, the Agency has also estimated the percent removals for antimony and total chromium by comparing the treated waste concentration for the selected BPT technology for those two toxic metals with the treated waste concentrations for the selected BAT technology for those same two pollutants. The calculation is as follows:

Antimony: BPT = 0.8 mg/l
BAT = 0.4 mg/l

Percent Removal = [(0.8 - 0.4) ÷ (0.8)] (100)
= 50%

Chromium (Total) BPT = 0.25 mg/l
BAT = 0.16 mg/l

Percent Removal = [(0.25 - 0.16) ÷ (0.25)] (100)
= 36%

The percent removals for total chromium are less than the removals achieved by 25% of the POTWs in the "50 Cities" study for chromium (65%). However, a portion of the total chromium is hexavalent chromium, which is removed poorly by a POTW. Federal Guidelines: State and Local Pretreatment Standards, Volume II, EPA 430/9-16-017b, January, 1977, page 6-51, states that the average hexavalent chromium removal for plants with biological treatment (i.e., secondary treatment) is 18%. Hexavalent chromium could interfere with the operation of the POTW, or be incorporated into the sludge and thus interfere with the POTW's chosen sludge disposal method. Information from the chrome pigments industry and the sodium dichromate industry indicates that filtration does remove some additional hexavalent chromium. Accordingly, since additional hexavalent chromium is removed by filtration, since the removal of hexavalent chromium by a POTW is small, and since hexavalent chromium is highly toxic, the Agency believes it is prudent to regulate the discharge of total chromium, which includes hexavalent chromium in discharges to POTW from sodium chlorate plants with pretreatment limitations based on the application of BAT technology.

There is only very limited data on the removal of antimony by a POTW available. The removals achieved by 25% of the POTWs in the "50 Cities" study for other toxic metals range from 19% to 66%. The removal of antimony by a POTW could be less than 50%. Therefore, the Agency believes it is prudent to regulate the discharge of antimony to POTW in the sodium chlorate industry with pretreatment limitations based on BAT technology.

Existing Sources

Since there are no indirect dischargers in this subcategory, the Agency is excluding this subcategory from categorical PSES under the provisions of paragraph 8(b) of the Settlement Agreement.

New Sources

The Agency is promulgating PSNS that are equal to NSPS because these standards provide for the removal of antimony and chromium, which would likely pass through a well operated POTW with secondary treatment in the absence of pretreatment. Pollutants regulated under PSNS are antimony and chromium. Chlorine is not regulated under PSNS because POTW influent is often chlorinated.

SECTION 15

REFERENCES

1. Coleman, John E., "Electrolytic Production of Sodium Chlorate," American Institute of Chemical Engineers Symposium Series 1981, vol. 77 (204), pp. 244-263.

2. Shreve, R. Norris and Brink, Joseph A. Jr., "Chemical Process Industries," McGraw-Hill, 1977.

3. U.S. Environmental Protection Agency, "Development Document for proposed Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category," EPA Report No. 440/1-79-007, June 1980.

4. JRB Associates, Inc., "An Assessment of pH Control of Process Waters in Selected Plants," Draft Report to the Office of Water Programs, U.S. Environmental Protection Agency, 1979.

SECTION 16

ZINC CHLORIDE INDUSTRY

INDUSTRIAL PROFILE

General Description

Zinc chloride is manufactured primarily for market use although some zinc chloride is used in the captive production of zinc ammonium chloride. Zinc chloride is used as an ingredient in dry cell batteries; oil well completion fluids; tinning; galvanizing and soldering fluxes; and for the preservation and flameproofing of wood. It is also used as a deodorant, and in disinfecting and embalming fluids. In chemical manufacturing, zinc chloride serves as a catalyst and as a dehydrating and condensing agent. Further uses include the manufacture of parchment paper, dyes, activated carbon and durable press fabrics and the printing and dyeing of textiles. The industry data profile is presented in Table 16-1.

There are seven known producers of zinc chloride of which five plants discharge wastewater directly, while two discharge indirectly.

Production in this subcategory is more than 25,000 tons per year, while total daily flow is in excess of 1,500 cubic meters.

General Process Description and Raw Materials

Zinc chloride is produced by reacting zinc metal with hydrochloric acid and concentrating the zinc chloride solution by evaporation. The general reaction is:

$$Zn + 2HCl = ZnCl_2 + H_2$$

Various forms of zinc feed material are used, from pure zinc metal to galvanizer skimmings. The latter may contain galvanizing fluxes, iron oxide, cadmium and lead in addition to the zinc metal. Galvanizing wastes may require milling and further processing prior to use in the zinc chloride manufacturing process. A zinc chloride solution is produced by the dissolution of the zinc feed with hydrochloric acid. The solution is generally purified by chemical addition to remove metal salts, then filtered and concentrated. The product is either marketed as a solution or further concentrated to yield a solid product. One facility utilizes a zinc chloride-containing process wastewater containing organic chemicals from an adjacent

TABLE 16-1. SUBCATEGORY PROFILE DATA FOR ZINC CHLORIDE

Number of Plants in Subcategory	7
Total Subcategory Production Rate	>25,000 kkg/yr
Minimum	<4.5 kkg/yr
Maximum	Confidential
Total Subcategory Wastewater Discharge	>1500 m^3/day
Minimum	26 m^3/day
Maximum	719 m^3/day
Types of Wastewater Discharge	
Direct	5
Indirect	2
Zero	0

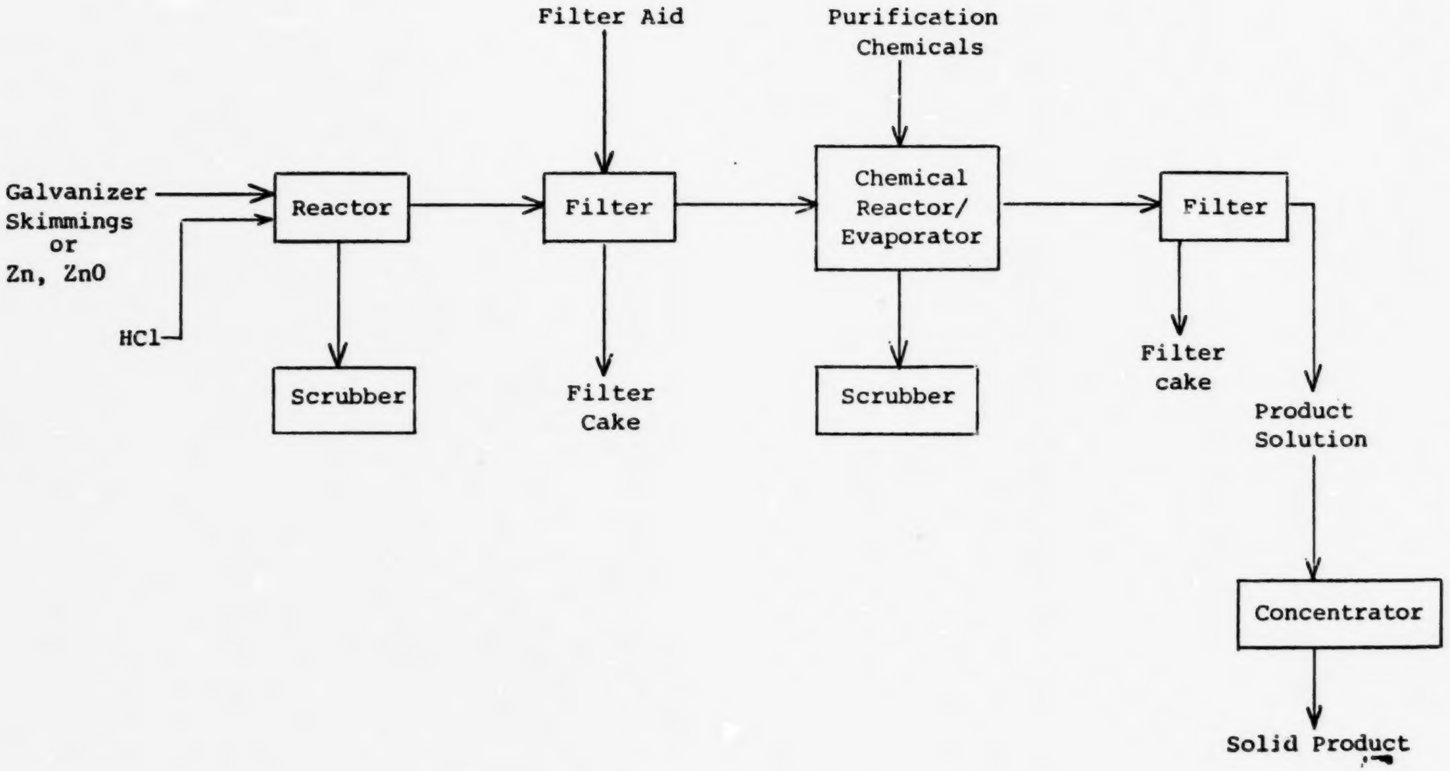

Filter Aid
Purification Chemicals
Galvanizer Skimmings or Zn, ZnO
HCl
Reactor
Filter
Chemical Reactor/ Evaporator
Filter
Scrubber
Filter Cake
Scrubber
Filter cake
Product Solution
Concentrator
Solid Product

FIGURE 16-1. GENERALIZED PROCESS FLOW DIAGRAM FOR ZINC CHLORIDE.

TABLE 16-2. WATER USAGE AT ZINC CHLORIDE FACILITIES(1)

	Flow (m^3/kkg of Zinc Chloride)				
	Plant Designation				
WATER USE	F125	F140	F120	F144	F143
Noncontact Cooling	0	0	0	0	5.73
Direct Process Contact	0	1.6	0.03	5.67	0
Indirect Process Contact	4.94	13.65	0.69	7.56	1.62
Maintenance	NA	0.03	0.05	0.05	0.42
Air Pollution Scrubbers	NA	0	1.38	0	3.33
Noncontact Ancillary	NA	0.32	0.10	NA	1.39
TOTALS	4.94	15.6	2.25	13.3	12.5

NA Flow volume not available.

1. Values indicated only for those plants that reported separate and complete information.

Source: Section 308 Questionnaires and Plant Visit Reports

TABLE 16-3. WASTEWATER AT ZINC CHLORIDE FACILITIES(1)

	Flow (m^3/kkg of Zinc Chloride)				
	Plant Designation				
WASTEWATER SOURCE	F125	F140	F120	F144	F143
Direct Process Contact	0	1.6	0	1.89	0
Indirect Process Contact	4.94	13.65	0.69(2)	7.56	1.62
Maintenance	NA	0	NA(2)	0.05	0.42
Air Pollution Scrubbers	NA	0	1.24(2)	0	3.33
TOTALS	4.94	15.3	1.93	9.5	5.37
Noncontact Cooling	0	0	0	0	5.73
Noncontact Ancillary	NA	0.032	0.01	NA	1.39
Storm Water	NA	NA (3)	7.14	0.53	2.67

NA Flow volume not available.

1. Values indicated only for those plants that reported separate and complete information.
2. Wastewater recycled within plant.
3. Stormwater unknown but not zero.

Source: Section 308 Questionnaires and Plant Visit Reports

facility as a raw material for zinc chloride production. The organic chemicals are removed from that wastewater before the zinc chloride solution is processed. Figure 16-1 shows a general process flow diagram for the manufacture of zinc chloride.

WATER USE AND WASTEWATER SOURCE CHARACTERIZATION

Water Use

Water is used primarily for air pollution control, in barometric condensers, equipment washdowns, pump seal maintenance, and as a reaction medium for the hydrochloric acid. Table 16-2 summarizes plant water use in the subcategory as determined from industry responses to the Agency's request for information under §308 of the Act and engineering visit reports.

Wastewater Sources

Generally, condensate from the evaporators used to concentrate the zinc chloride product solution and blowdown from the cooling of the barometric condenser water constitute the major wastewater streams. These streams are combined with wastewater from air pollution scrubbers, equipment washdowns, pump seal leaks and, in some cases, other product processes and treated before discharge or recycle. Table 16-3 identifies the various wastewater streams and related daily flows for those zinc chloride plants which supplied complete data. Storm water can contribute significant additional water flow to the treatment facility at several plants.

DESCRIPTION OF PLANTS VISITED AND SAMPLED

Five plants (F118, F120, F140, F144 and F145) producing zinc chloride were visited during the course of the program. In addition, wastewater sampling was conducted at Plants F120 and F144. One of these plants, plant F120, no longer produces zinc chloride and is therefore not counted as one of the existing seven plants.

Plants Sampled

Plant F120 produced zinc chloride and a number of other inorganic products, but has since discontinued zinc chloride production. At the time of sampling, the plant produced a zinc chloride solution by the reaction of zinc-containing waste materials (galvanizer skimmings) with hydrochloric acid. A wet scrubber used to minimize hydrochloric acid emissions generated a dilute acid waste. Solids from the batch reactor were hauled to an approved landfill site. The zinc chloride solution was then

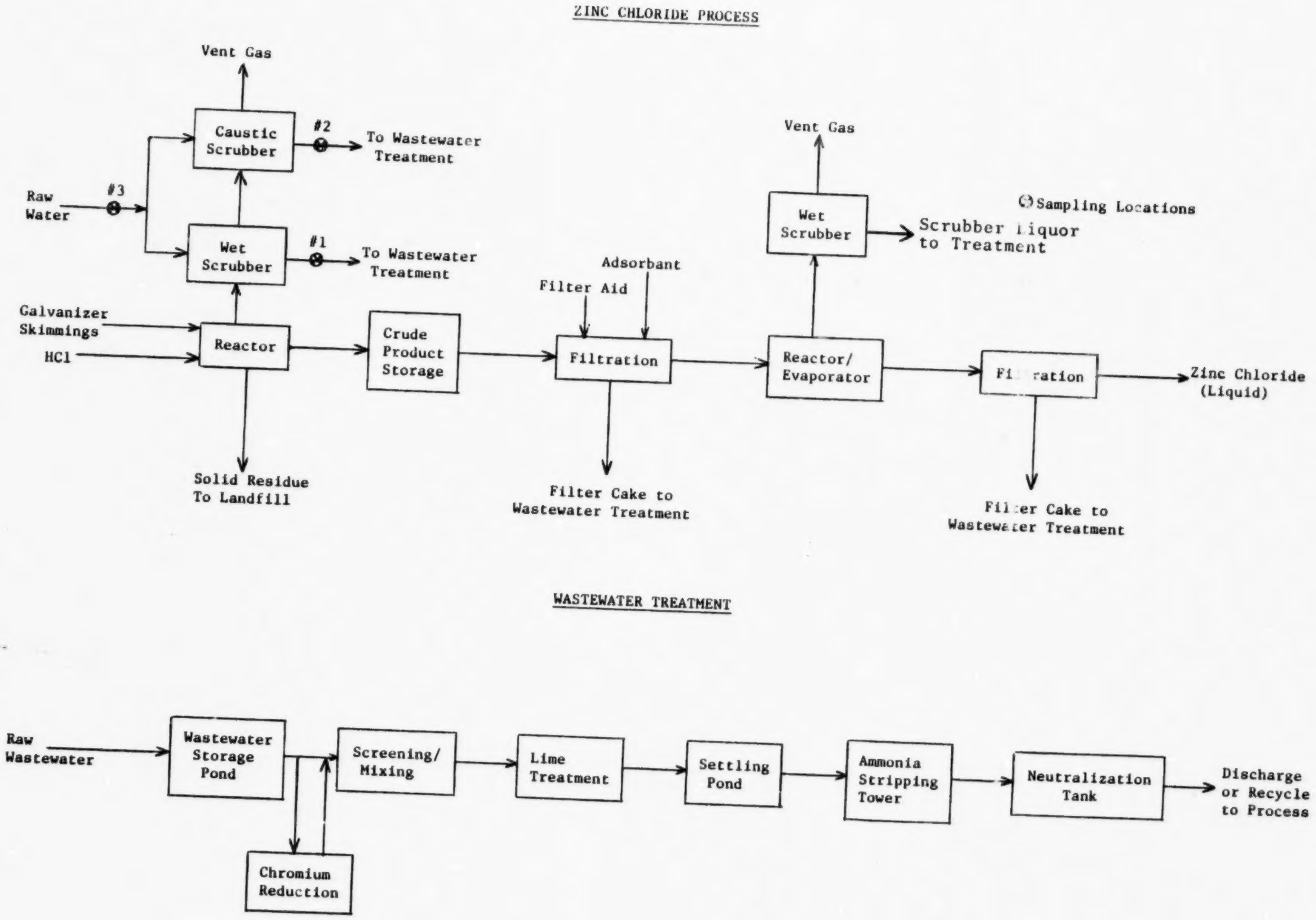

ZINC CHLORIDE PROCESS
Vent Gas
Caustic Scrubber
#2
To Wastewater Treatment
Raw Water
#3
Wet Scrubber
#1
To Wastewater Treatment
Galvanizer Skimmings
HCl
Reactor
Solid Residue To Landfill
Crude Product Storage
Filter Aid
Adsorbant
Filtration
Filter Cake to Wastewater Treatment
Vent Gas
Wet Scrubber
Scrubber Liquor to Treatment
Sampling Locations
Reactor/ Evaporator
Filtration
Zinc Chloride (Liquid)
Filter Cake to Wastewater Treatment
WASTEWATER TREATMENT
Raw Wastewater
Wastewater Storage Pond
Chromium Reduction
Screening/ Mixing
Lime Treatment
Settling Pond
Ammonia Stripping Tower
Neutralization Tank
Discharge or Recycle to Process

FIGURE 16-2. PROCESS WASTEWATER TREATMENT AND SAMPLING LOCATIONS FOR PLANT F120.

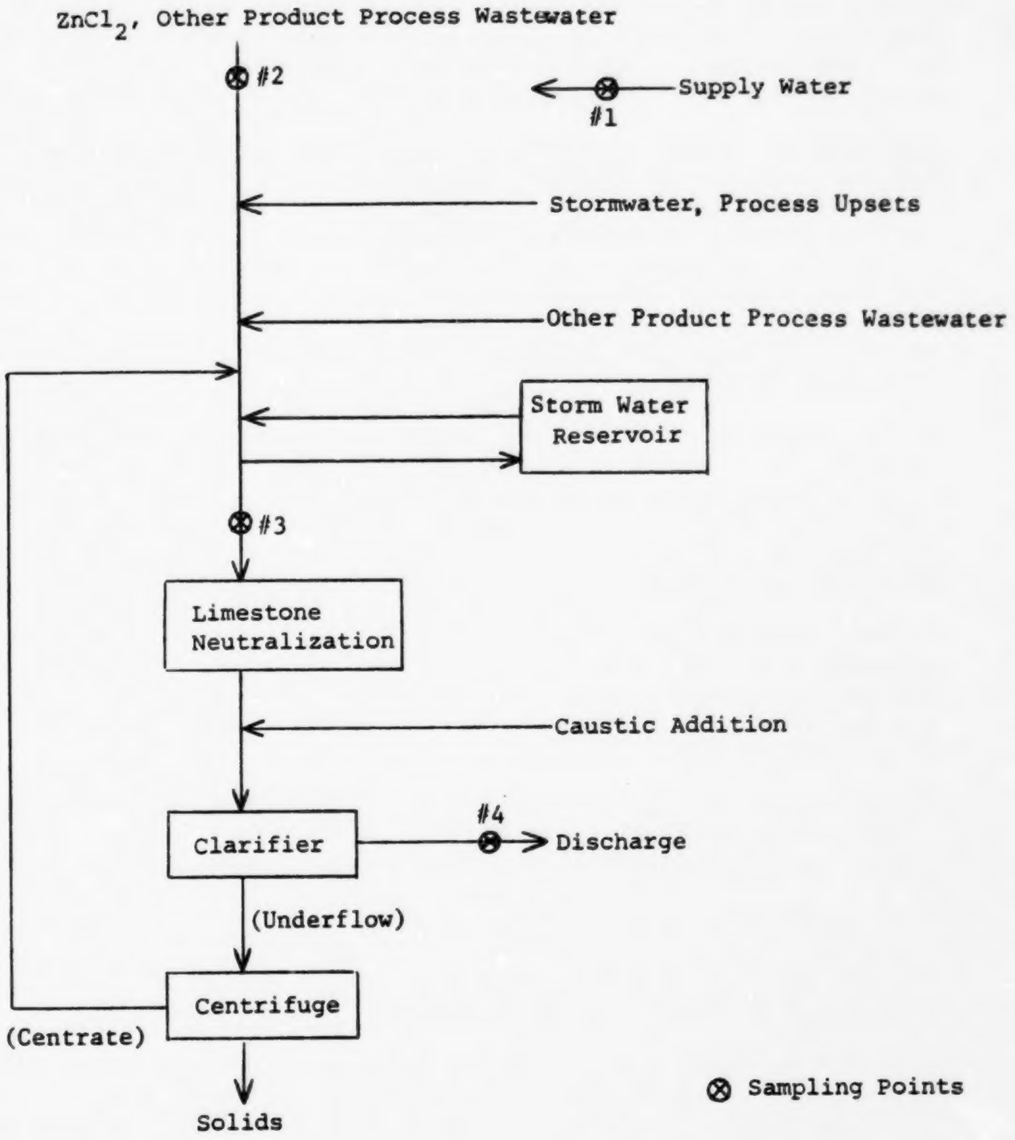

ZnCl2, Other Product Process Wastewater
#2
Supply Water
#1
Stormwater, Process Upsets
Other Product Process Wastewater
Storm Water Reservoir
#3
Limestone Neutralization
Caustic Addition
Clarifier
#4
Discharge
(Underflow)
Centrifuge
(Centrate)
Solids
Sampling Points

FIGURE 16-3. WASTEWATER TREATMENT PROCESS AND SAMPLING LOCATIONS FOR PLANT F144.

separated from unreacted materials and purified by chemical additives to remove iron and manganese salts. The precipitated salts were filtered and a solution grade product was marketed. The filter residue was slurried to the in-plant treatment system. An additional wet scrubber stream resulted from the purification/evaporation stage.

Wastewater from scrubbers, equipment washdowns, pump seal leaks and various other product processes were combined, treated with lime and lagooned. The treated wastewater was used to slurry the purification and treatment sludges back to the settling ponds for temporary storage. At the time of sampling, there had been no discharge of process wastewater streams in one and a half years. Since the lagoons are unlined, percolation of part of the wastewater into the subsoil could account for the fact that there has been no discharge.

Solid waste generated from rotary vacuum filtration of the crude product and from filtration of the crude after treatment to remove impurities is slurried with the recycled wastewater as described above and treated with lime to pH 10. Solids are allowed to settle, and the supernatant is air stripped for ammonia removal prior to recycle or discharge (optional).

Three streams at Plant F120 were identified for sampling. These streams included the wet scrubber discharge, caustic scrubber discharge, and raw water used for make-up. Figure 16-2 illustrates a process flow diagram and associated sampling locations at Plant F120.

Plant F144 produces zinc chloride from the reaction of zinc crudes with hydrochloric acid. The zinc crudes contain zinc metal, galvanizing fluxes, iron oxide, cadmium and lead.

The process involves the milling and classifying of the crudes, dissolution in hydrochloric acid, and concentration, purification and filtration steps considered proprietary. The product may be sold as a solution or as a solid product.

Wastewater sources from the zinc chloride process include purge from the barometric condenser, condensate from steam concentrators, washout waters and accidental leaks and spills. Solid residues with entrained liquid are sent to a landfill. Process wastewater from the zinc chloride operation is combined with other process wastewaters and fed to a pair of dolomitic limestone neutralizers where the pH is raised to a range of 5-6. Caustic is then added to adjust the pH to 8.8-8.9 and the wastewater is sent through a clarifier before discharge. Sludge from the clarifier is sent to a centrifuge. Solids are collected and the centrate is recycled to the beginning of the process. Plant F144 also has a large wastewater impoundment facility to contain excess runoff during storms, process upsets, and other wastewater flows during preventive maintenance at the treatment facility. The water in the holding pond is discharged through the treatment plant when process wastewater flows are reduced.

Streams sampled at Plant F144 included the intake water, plant raw wastewater (which contained the zinc chloride process wastewater), combined plant raw wastewater with raw wastewater from other products produced at the facility, and treated clarifier effluent. Figure 16-3 presents a schematic of the wastewater treatment process and the sampling points.

Table 16-4 presents flow data, total suspended solids (TSS), zinc, arsenic, lead and antimony concentrations for the sampled wastewater streams.

Treatability Study Conducted at Zinc Chloride Plant F144

Treatability experiments were conducted in April 1984 at zinc chloride Plant F144 to develop additional information on the application of filtration technology in the zinc chloride subcategory. (See the contractor's report entitled "Dual-Media Filtration Test Results at Zinc Chloride Plant F144", which is a part of the record for this rulemaking.) A pilot-scale dual-media filtration system (Level 2) was tested on-site over a three day period. Filtration was evaluated as an end-of-pipe technology. The wastewater at Plant F144 is subject to Level 1 technology in the existing treatment plant, and the effluent from that treatment was used as the influent to the pilot-scale treatment system.

The filter media used during the tests at Plant F144 were silica sand and anthracite coal, which are typical media normally used in dual-media filters. A schematic of the pilot-scale filtration system is shown in Figure 16-4. The tests were run for eight hours per day over a three day period, which nine influent and effluent samples collected in each eight hour period, one each hour. All tests ran the full eight-hours because no breakthrough of the filters occurred. The three different hydraulic loadings tested were 4.5 gpm/ft^2, 7.3 gpm/ft^2, and 10.2 gpm/ft^2. The three flow rates were tested to better characterize the filtration efficiencies, and determine if higher flow rate filters, which are cheaper than low rate filters, would provide adequate removals of zinc.

The test was designed to determine the efficiency of filtration in removing TSS and total zinc from effluent from Level 1 treatment. Plant F144 is achieving excellent removals of lead, consequently lead in the wastewater was monitored only to determine if the lead levels were abnormally high during the test period. The less sensitive 304(h) method (flame atomic absorption) was believed to be adequate for this purpose, rather than the heated graphite atomizer method. Arsenic was also monitored to gather additional data, although limited data at Plant F144 suggested that arsenic levels would be very low in treated effluent. Dissolved zinc was monitored because the plant has historically monitored dissolved zinc. Turbidity was monitored on-site as a rapid check on breakthrough of the filters. We also monitored pH, and collected a sample of the solids collected on the filter for analysis of total zinc content as a quality control check for the analysis of zinc in the wastewater, because the calculated amount of zinc removed (from comparing influent and effluent total zinc analyses) should equal the amount of zinc collected by the filter. In summary, the pollutant parameters monitored in influent and effluent samples were TSS, total zinc, dissolved zinc, total lead, total arsenic, pH, and turditity.

The results of the tests for TSS and total zinc are shown in Table 16-5. These data demonstrate that the filter is very efficient in removing TSS and total zinc, with average TSS removal of about 95 percent and average total zinc removal of about 90 percent. The minimum total zinc removal was 80.7 percent. No break through of the filter, which would be shown by high levels of TSS, was observed.

As expected from historical data, the lead discharges are well controlled by the Level 1 treatment system at this plant, and all values were less than 0.1 mg/l, the typical detection limit for the flame atomic absorption method used. The heated graphite atomizer, the more sensitive 304(h) method, could have been used to provide lower detection limits, although, as noted above, lead analyses during this test were used only to determine if the lead levels were significantly higher than the historic values. All arsenic values were reported as less than 0.003 mg/l using 304(h) methods which indicates that, during the three days of the test, arsenic levels were quite low.

Plant F144 split several samples with us and has provided their results to us. These results are shown in Table 16-5A. These results are similar to our results although the plant took less than half as many samples and consequently their data could be misinterpreted. For example, the last samples analyzed by Plant F144 on days 1 and 2 of the test show higher levels of total zinc than the previous samples for those days, which might indicate breakthrough. However, our later samples show the total zinc and

TSS levels decreased; Plant F144 shows no analytical results for those later samples.

Plant F144 lead analyses were more sensitive than our analyses. Their data shows that lead is removed efficiently by the filter, even when the lead in the influent to the filter is less than 0.1 mg/l. Plant F144 data also shows arsenic at measurable levels. We do not know the reason for the difference between our results for arsenic and the Plant F144 results, but both sets of data show arsenic levels much less than 0.5 mg/l.

Other Plants Visited

Plant F118 combines zinc metal with hydrochloric acid to yield a zinc chloride solution. The solution is diluted with water to the desired concentration for sale. Wastewater generated in this process consists of spills and maintenance washdowns. The zinc chloride wastewater is combined with wastewaters from all other products and treated with alkaline precipitation and clarification before discharge to a receiving stream.

Plant F140 receives process wastewater from an adjacent facility as a raw material for zinc chloride production. The wastewater contains zinc chloride along with other metal impurities and organic wastes. The process water is treated to remove organics. Metal impurities are then removed by pH adjustment using zinc carbonate, and filtration. The process water may be strengthened first by addition of zinc and hydrochloric acid and then purified. The solution is then concentrated by evaporation to the desired strength.

All wastewater streams (blowdown resulting from cooling of barometric condenser water, precipitation run-off, leaks, spills, and pump seal water) are collected and pumped to a holding tank where the pH is raised to about 7. The neutralized wastewater is allow to settle before discharge to a river and the settled sludge is recycled to the production process.

Plant F145 produces a variety of inorganic and organic chemicals. Zinc chloride is produced by combining zinc metal or zinc oxide with hydrochloric acid. All zinc chloride wastewater, including scrubber water and any process water which cannot be recycled, is sent to the wastewater treatment facility which receives both organic and inorganic streams from all plant production processes. The wastewater is equalized, subjected to lime precipitation at pH 9.5-10.2, agitated and clarified. The sludge from the clarifiers is dewatered and disposed as solid waste. The overflow from the clarifiers receives biological treatment before being discharged directly to a receiving stream.

TABLE 16-4. POLLUTANT CONCENTRATIONS AND LOADS FOR SAMPLED ZINC CHLORIDE FACILITIES(1)

Stream No.	Stream Description	TSS	Zn	Cd	Pb	Cr
				mg/l kg/kkg		
				Plant F120		
1	Wet Scrubber	52 0.0717	223 0.307	0.109 0.00015	1.80 0.00248	0.082 0.00011
2	Caustic Scrubber	1020 1.41	0.147 0.00019	0.028 0.000039	1.867 0.00273	0.21 0.00029
				Plant F144		
2	Raw Wastewater	38.3 0.886	184.7 4.27	0.032 0.000740	0.107 0.00248	0.52 0.0120
3	Combined Raw Wastewater	26.7 1.21	240.8 10.9	0.125 0.00567	0.415 0.0188	3.067 0.139
4	Clarifier Effluent	11.7 0.884	1.0 0.0756	<0.010 <0.00076	0.004 0.00030	0.079 0.0060

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(1) Concentrations and loads represent the average of three daily samples.

Table 16-5. Results of the Environmental Protection Agency's Dual-Media Filtration Tests at Plant F144 (all values mg/l).

	TSS Results			Zinc Results		
	Influent	Effluent	TSS Removal (%)	Influent	Effluent	Total Zinc Removal (%)
Day 1 (4.5 gpm/ft^2)						
1*	7.60	0.30	96.1	4.53	0.27	94.0
2	8.15	0.52	93.6	4.62	0.20	95.7
3	7.63	0.74	90.3	4.60	0.34	92.6
4	8.07	0.44	94.5	4.48	0.64	85.7
5	7.48	0.15	98.0	4.12	0.69	83.3
6	6.44	0.30	95.3	4.02	0.75	81.3
7	5.70	0.30	94.7	3.57	0.69	80.7
8	5.63	0.15	97.3	3.44	0.41	88.1
9	5.19	0.44	91.5	3.31	0.52	84.3
Average	6.88	0.37	94.6	4.08	0.50	87.3
Day 2 (7.3 gpm/ft^3)						
1*	12.00	0.37	96.9	7.38	0.45	93.9
2	11.78	0.44	96.3	8.19	0.50	93.9
3	11.56	0.37	96.8	7.26	0.58	92.0
4	11.56	0.52	95.5	7.38	0.54	92.7
5	10.96	0.15	98.6	7.11	0.59	91.7
6	9.48	0.67	92.9	6.33	0.65	89.7
7	8.89	1.11	87.5	6.54	0.69	89.4
8	9.70	0.81	91.6	7.11	0.76	89.3
9	10.59	0.96	90.9	7.44	1.18	84.1
Average	10.72	0.60	94.1	7.19	0.66	90.7
Day 3 (10.2 gpm/ft^2)						
1*	7.63	0.07	99.1	4.36	0.41	90.6
2	7.33	0.30	95.9	4.33	0.30	93.1
3	7.63	0.30	96.1	4.24	0.42	90.1
4	7.33	0.52	92.9	4.27	0.45	89.5
5	7.85	0.15	98.1	4.27	0.47	89.0
6	9.11	0.37	95.9	4.91	0.46	90.6
7	11.86	0.44	96.3	4.82	0.42	91.3
8	9.63	0.52	94.6	5.02	0.41	91.8
9	10.00	0.96	90.4	5.37	0.46	91.4
Average	8.71	0.40	95.5	4.62	0.42	90.8

*Initial Value. Samples taken every hour during the test.

Table 16-5A Plant F144 Results for Split Samples of Dual-Media Filtration Tests

	TSS Results			Zinc Results		
	Influent	Effluent	TSS Removal (%)	Influent	Effluent	Total Zinc Removal (%)
Day 1 (4.5 gpm/ft²)						
1	No samples taken			5.2	0.73	86.0
2				-	-	-
3				5.1	0.88	82.7
4				-	-	-
5				4.3	1.38	67.9
6				-	-	-
7				-	-	-
8				-	-	-
9				-	-	-
Average				4.87	0.99	78.9*
Day 2 (7.3 gpm/ft²)						
1	No samples taken			9.3	1.5	83.9
2				-	-	-
3				8.3	1.2	85.5
4				-	-	-
5				-	-	-
6				7.0	3.4	51.4
7				-	-	-
8				-	-	-
9				-	-	-
Average				8.2	2.03	73.6*
Day 3 (10.2 gpm/ft²)						
1	7.2	1.0	86.1	4.7	0.8	82.9
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	6.8	1.6	76.5	3.0	0.8	73.3
5	7.2	1.0	86.1	4.4	0.9	79.5
6	8.6	0.8	90.7	5.1	0.9	82.3
7	10.0	0.8	92.0	5.1	0.7	86.2
8	10.4	1.0	90.4	5.2	0.7	86.5
9	-	-	-	-	-	-
Average	8.37	1.03	87.0	4.58	0.8	81.8*

*Averages may not agree with influent/effluent averages because of rounding.

Summary of Toxic Pollutant Data

Eleven toxic metals were found at detectable concentrations in the raw wastewater at the two sampled plants. Two toxic organic pollutants were found in untreated wastewater at concentration levels greater than 0.010 mg/l (10 ug/l). One of these, methylene chloride, was found in high concentrations in the raw wastewater of Plant F144. There is no known source for the methylene chloride at the plant and its presence in the wastewater was not be confirmed by resampling. The most probable explanation is contamination of sampling equipment or containers or an erroneous laboratory determination.

The maximum concentrations observed in the raw wastewater at the two sampled plants are presented below:

Pollutant	Maximum Concentration Observed* (ug/l)
Antimony	1,869
Arsenic	14,170
Cadmium	95
Chromium	640
Copper	350
Lead	2,100
Nickel	1,205
Selenium	6
Silver	165
Thallium	485
Zinc	490,000
Chloroform	521
Methylene Chloride	430,000

*Maximum daily observed concentrations for antimony, arsenic, cadmium, copper, lead, nickel, silver, and thallium were obtained from daily flow-proportioned averages for the two wastewater streams at Plant F120.

Section 5 of this report describes the methodology of the sampling program. In the zinc chloride industry, a total of six days of sampling were conducted at Plants F120 and F144. Five wastewater streams were sampled and analyzed. The evaluation of toxic metal pollutants in these streams was based on 195 analytical data points. In Table 16-5, the toxic pollutant raw

TABLE 16-6. TOXIC POLLUTANT RAW WASTE DATA FOR SAMPLED ZINC CHLORIDE FACILITIES

Average Daily Pollutant Concentrations and Loads

$\frac{\text{mg/l}}{\text{kg/kkg}}$

	Plant Designation		
Pollutant	F120	F144	Overall Average
Antimony	1.435 0.00396	0.045 0.00104	0.74 0.00250
Arsenic	5.605 0.0155	<0.006 0.00014	<2.81 0.00782
Cadmium	0.069 0.00019	0.032 0.00074	0.05 0.00047
Chromium	0.146 0.00040	0.520 0.0121	0.333 0.00625
Copper	0.279 0.00077	0.067 0.00155	0.173 0.00116
Lead	1.834 0.00506	0.107 0.00248	0.854 0.00377
Nickel	1.049 0.00289	0.017 0.00039	0.533 0.00164
Silver	0.142 0.00039	<0.001 0.00002	<0.071 0.00021
Thallium	0.325 0.00090	<0.100 0.00232	<0.213 0.00161
Zinc	111.724 0.308	184.700 4.29	148.200 2.3

waste data are presented as the average daily concentrations found at the sampled plants.

POLLUTION ABATEMENT OPTIONS

Toxic Pollutants of Concern

The principal pollutant of concern is zinc. Other pollutants found in significant concentrations in the process wastewaters are probably related to the purity of the zinc metal and acid sources. The toxic metals arsenic, antimony, lead, chromium and nickel found during screening and verification sampling likely originate as constituents of the galvanizer skimmings used as the raw zinc material. Highest concentrations of these metals were found primarily in the scrubber wastewater streams from Plant F120. The scrubber step preceeds the heavy metals removal step noted in several other plant processes. Therefore, such high levels of the above-mentioned heavy metals would not be expected unless a facility's operations included scrubbing of the Zn/HCl reactor gases.

Existing Wastewater Control and Treatment Practices

Treatment practices at the visited plants were presented earlier. Available information on treatment practices at other plants are presented below.

Plant F125 produces other inorganic salts in addition to zinc chloride. Wastewater from all processes is treated in a system consisting of equalization, pH adjustment with caustic, and sedimentation in a series of lined and unlined impoundments before discharge to a receiving stream. Solid wastes are hauled to a chemical landfill.

Plant F143 produces zinc chloride using zinc oxide, zinc powder and brass skimmings as raw materials. Wastewater from the process is neutralized before discharge to a POTW.

Plant F126 produces zinc chloride in small quantities. The company reported that no process wastewater was discharged from the process.

Other Applicable Control/Treatment Technologies

Although some plants only neutralize their wastes before discharge, the primary method of wastewater treatment in the zinc chloride industry is precipitation and clarification or sedimentation of process wastes. Another technology which would be applicable to this industry is filtration for further solids and toxic metal removal.

Process Modifications and Technology Transfer Options

A reduction in the volume of process contact wastewater generated might be achieved by recycling all direct process contact wastewater where possible. For example, several facilities employ recycle of scrubber water with only a small volume of blowdown necessary. Condensate from product concentration and crystallization appears to be another wastewater source with potential for recycle. The principle difference between plants with high water use and those with low water use is that the latter use pure raw materials and sell solution grade zinc chloride only. This is an economic decision not a technology per se. One existing zinc chloride manufacturer reported that it has no discharge of process wastewater from the very small quantities of zinc chloride produced at its plant.

Sludge volumes may be reduced by the use of caustic soda instead of lime for wastewater treatment. This practice offers other advantages including reduced scale formation and faster reaction times.

Best Management Practices

If contact is possible with leakage, spillage of raw materials, or product, all storm water and plant site runoff must be collected and directed to the plant treatment facility. This contamination can be minimized by indoor storage of chemicals and proper air pollution control.

If solids from the wastewater treatment plant are disposed or stored on-site, provision must be made to control leachates and permeates. Leachates and permeates which contain toxic pollutants should be directed to the treatment system for further treatment.

Advanced Treatment Technology

Zinc-containing residues such as galvanizing wastes and zinc dusts are often used as raw materials for zinc chloride production. These materials contain a variety of toxic and non-toxic metals such as lead, zinc, cadmium, iron and manganese. The manufacturing process removes much of these metals from the zinc chloride product in the form of filter cake. Other constituents can be transmitted to the wastewater. Further reduction of metals would require treatment by granular media filtration.

One facility producing zinc chloride from an organic wastewater stream generated at a nearby chemical manufacturing complex may require treatment technology in addition to the levels considered here. The water is treated to remove organics as part of the manufacturing process, but no data is available on the amount of toxic organics in the wastewater. Elevated COD and the presence of toxic organics would be pollutants which could occur at this facility. The presence of these additional pollutants are not expected to affect the effectiveness of treatment for metals removals, as a similar situation occurs at Plant F145 which provides effective treatment for removal of metals.

Selection of Appropriate Technology and Equipment

Technologies for Different Treatment Levels

A. Level 1

Level 1 treatment consists of alkaline precipitation, clarification or settling, and dewatering of the sludge in a filter press. This technology is illustrated in Figure 10-10. A holding basin sized to retain 4-6 hours of flow is provided.

The initial treatment step is the addition of lime or caustic soda. This is followed by clarification/settling (if the wastewater characteristics are suitable, a tube settler may be substituted for a clarifier to save space). Sludge is removed from the clarifier and directed to a filter press for dewatering. Pits are provided at the filter press for the temporary storage of sludge. The sludge is periodically transported to a hazardous material landfill. A monitoring system is installed at the discharge point. The objective of Level 1 technology is to remove heavy metals and suspended solids.

Level 1 treatment was selected as the basis for BPT because it represents a typical and viable industry practice for the control of suspended solids, arsenic, lead and zinc. All of the direct dischargers have Level 1 treatment or equivalent already installed.

B. Level 2

Level 2 treatment consists of the addition of granular media filtration following clarification in the Level 1 treatment system. The granular media filtration technology is illustrated in Figure 10-11. Level 2 technology has been selected as a means of achieving improved removal of metal hydroxide precipitates and other suspended solids because our treatability study shows that this technology gives excellant results when transferred to this industry. Currently no plants in this subcategory employ granular media filtration for wastewater treatment.but plant F145 is achieving the limitations.

Equipment for Different Treatment Levels

A. Equipment Functions

Conventional sludge dewatering by a filter press is used for sludge removed by the clarification/settling system. The sludge from the filter press is disposed of off-site in a hazardous material landfill. If a tube settler is used, backwash from the settler is returned to the influent holding basin. Likewise, if granular media filters are used, backwash water is returned to the influent holding basin. All equipment is conventional and readily available.

B. Chemical Handling

Caustic soda (50 percent NaOH) is used to precipitate heavy metals in Level 1 at most plants. However, lime precipitation may be used at large plants due to the quantity and cost of alkaline reagent required. Precipitation of zinc is best at a pH of about 9, and occasional pH discharges above 9 could occur. For this reason, and recognizing that regulations for other industries allow pH range up to 10, the pH limitations have been revised in the final rules from the proposed levels of 6-9 and are now 6-10. Therefore, readjustment of pH will not be necessary.

C. Solids Handling

Treatment sludges generated by Level 1 are dewatered in a filter press. The solids would be disposed of off-site in a hazardous material landfill. Level 2 filter backwash may be sent to the head of the plant or, if the solids concentration is sufficiently high, may be sent directly to the filter press.

Treatment Cost Estimates

As stated earlier in this section, there are seven known producers of zinc chloride, five of which are direct dischargers of wastewater. The average wastewater generation in the industry was thought to be 10.5 m^3/kkg, but this included some plants using pure zinc or zinc oxide and selling solution grade product only. The zinc chloride model plant used for the proposed regulations has a unit flow of 13.5 m^3/kkg. However, recent data indicate that unit flow may vary considerably depending upon the product produced (liquid or solid). Because this is determined

TABLE 16-7. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Zinc Chloride

ANNUAL PRODUCTION: 26,000 METRIC TONS

DAILY FLOW: 3,785 CUBIC METERS (1,000,000 GPD)

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1	2	3	4	5
Facilities	152.9	-			
Installed Equipment (Including Instrumentation)	703.0	105.1			
Engineering	171.2	21.0			
Contractor Overhead and Profit	154.1	18.9			
Contingency	118.1	18.5			
Land	3.6	-			
Total Invested Capital	1,302.9	159.5			
Annual Capital Recovery	211.4	26.0			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	300.8	44.5			
Residual Waste Disposal	31.7	0.9			
Total Annual Cost	543.9	71.4			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, sludge dewatering

LEVEL 2: Filtration

TABLE 16-8. WATER EFFLUENT TREATMENT COSTS FOR MODEL PLANT.

SUBCATEGORY: Zinc Chloride

ANNUAL PRODUCTION: 5,700 METRIC TONS

DAILY FLOW: 260 CUBIC METERS

PLANT AGE: NA YEARS PLANT LOCATION: NA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEI				
	1	2	3	4	5
Facilities	21.6	-			
Installed Equipment (Including Instrumentation)	142.7	44.0			
Engineering	32.9	8.8			
Contractor Overhead and Profit	29.6	7.9			
Contingency	22.7	6.1			
Land	-				
Total Invested Capital	249.5	66.8			
Annual Capital Recovery	40.6	10.9			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	95.6	18.0			
Residual Waste Disposal	2.1	0.1			
Total Annual Cost	138.3	29.0			

b. TREATMENT DESCRIPTION

LEVEL 1: Alkaline precipitation, clarification, sludge dewatering

LEVEL 2: Filtration

by the market and cannot be predicted, we are promulgating guidelines and standards on a concentration basis only. Permit writers may convert the concentration-based limit to a mass-based limit based on the flow at individual plants.

Costs for two model plants were developed because of the wide variation of plant sizes in this subcategory. The annual productior rates used were 26,000 kkg and 5,700 kkg. The wastewater flows used were 3,785 m^3/day and 260 m^3/day respectively. Costs for the smaller plant were developed on the basis of the same wastewater characteristics as for the large plant to represent many plants which produce smaller quantities of the chemical. Chemical usage and sludge production were proportioned based upon flow but the small plant was assumed to use caustic soda while the large plant was assumed to use lime. Lime is cheaper but produces considerably more sludge, which cannot economically be reclaimed for zinc. Caustic produces less sludge and, when pure zinc is used (as is often the case for small plants), the sludge can be recovered for reclamation of the zinc.

Chemical reagent usage for wastewater treatment at the two model plants are estimated as follows:

	Large Plant	Small Plant
$Ca(OH)_2$	400 kg/day	88 kg/day (1)

Total solid waste generated is estimated as follows (Level 2 listings are incremental amounts):

Level	Solid Waste Large Plant	Small Plant
(1)	0.39 m^3/day	0.086 m^3/day
(2)	0.011 m^3/day	0.0024 m^3/day

Model Plant Treatment Costs. On the basis of model plant specifications and design concepts presented earlier and in Section 10, the estimated costs of treatment for two models with two levels are shown in Tables 16-7 and 16-8. The cost of Level 2 is incremental to Level 1.

Basis for Regulations

Basis for BPT Limitations

A. Technology Basis

For BPT, the Agency is setting limitations based upon alkaline precipitation and clarification, and dewatering of the sludge in a filter press. Of the five direct dischargers in this subcategory, all have this technology or equivalent installed.

B. Flow Basis

The limitations have been developed on a concentration basis only.

C. Selection of Pollutants to be Regulated

The selection of pollutants for which specific effluent limitations are being established is based on an evaluation of the raw wastewater data from screening and verification, consideration of the raw materials used in the process, literature data, historical discharge monitoring reports and permit applications, and the treatability of the toxic pollutants.

Tables 8-1 through 8-14 summarize the achievable concentrations of toxic metal pollutants from the literature using available technology options, data from other industries, and treatability studies. Water use and discharge data are presented earlier in this section together with generalized process characteristics. Pollutant concentrations of raw wastewater streams and a summary of maximum concentrations observed of toxic pollutants detected during screening and verification sampling at several plants are also presented earlier in this section. Data from Appendix A on the performance of in-place industry treatment systems was also utilized in developing the list of pollutants to be regulated.

Based upon the occurrence of treatable levels of specific toxic metals, arsenic, lead, and zinc were selected as candidate toxic pollutants for BPT regulations. Antimony, cadmium, chromium, copper, nickel, selenium, silver, and thallium were detected but at less than treatable levels.

Consideration of the raw wastewater concentrations presented earlier, industry data, and information in Section 8 related to the effectiveness of hydroxide precipitation, and clarification leads to the selection of arsenic, lead, and zinc as toxic pollutants to be regulated.

D. Basis of BPT Pollutant Limitations

Limitations are presented on a concentration (mg/l) basis only.

BPT limitations, which apply to all process wastewater discharged, are presented in Table 16-9.

1. Conventional Pollutants

a. pH

The treated effluent is to be controlled within the range of 6.0 - 10. This limitation is based upon the data presented in Appendix B of the Development Document for Proposed Effluent Guidelines for Phase I Inorganic Chemicals (Ref. 1) and the JRB study (Ref. 2). Zinc removal is best at a pH of about 9, and the effluent from treatment could be above 9 occasionally, unless additional effluent pH control is provided. For a large plant, the costs for compliance with the effluent pH of 6-9 would be $110,000 capital costs and over $20,000 annualized costs. Because no significant environmental impact is expected from effluent at a pH of 10, and because other industries allow effluent pH at a pH of 10, we believe a pH of up to 10 should be allowed for the zinc chloride subcategory.

b. TSS

Three Phase II plants (F125, F115 and F140) considered to be efficently operating their wastewater treatment facilities provided long-term Level 1 treatment system performance data for TSS. TSS data from Plant F144 were not used because the wastewater is passed through a limestone bed in the first stage of the plant's neutralization system. This would reduce the TSS loading to the clarifier giving lower TSS results than expected for the average inorganic chemicals plant. Since no other data from well-operated Level 1 treatment systems was available, and since the clarification provided at Plants F125, F115 and F140 for TSS removal would be similar to that necessary for TSS removal at zinc chloride plants (Plants F125 and F140 are zinc chloride plants), the BPT limitations for TSS are based upon the average of long-term averages calculated from data collected at Plants F125, F115 and F140. The long-term average of 13 mg/l was used to develop discharge limitations. Variability factors of 1.9 for a monthly average and 3.3 for a 24-hour maximum were used yielding TSS concentration limitations of 25 mg/l and 43 mg/l respectively. (See Section 15, BPT Limitations, for derivation of the variability factors.)

2. Toxic Pollutants

a. Arsenic

Since there is no long-term treatment system performance data for arsenic from any zinc chloride manufacturing plant, the BPT limitations for arsenic are based on estimated maximum 30-day averages achievable with Level 1 treatment taken from Table 8-11, and variability factors computed from long-term data for dissolved zinc at Plant F144 presented in Appendix A. Using a value of 0.5 mg/l as a long-term average, 2.0 as a variability factor for 30-day average computations, and 6.0 as a variability factor for 24-hour maximum computations, concentration limitations of 1.0 mg/l (30-day avarage) and 3.0 mg/l (24-hour maximum) are obtained.

b. Lead

Long-term performance data for lead is available for Plants F140 and F144. The data for Plant F144 show very low effluent lead levels, and the data are considered to be typical of Level 2 performance for lead in the zinc chloride subcategory rather than Level 1 performance. Consequently, we did not use Plant F144 data for lead limitations for BPT, although we did use that data for lead limitations for BAT. Plant F140 has an in-plant lead removal system which is not part of Level 1 treatment and is not typical of the industry. Therefore, we also did not use Plant F140 data for lead limitations for BPT. Because there are no long-term performance data for lead from any other zinc chloride plant with Level 1 treatment, the BPT limitations for lead are based on estimated 30-day averages achievable with Level 1 treatment taken from Table 8-11, and variability factors for dissolved zinc computed from long-term data at Plant F144 presented in Appendix A. Using a value of 0.3 mg/l as a long-term average, 2.0 as a variability factor for 30-day average computations, and 6.0 as a variability factor for 24-hour maximum computations, concentration limits of 0.6 mg/l (30-day average) and 1.8 (24-hour maximum) are obtained.

c. Zinc

The BPT limitations for zinc are based on long-term monitoring data from Plant F140 presented in Appendix A. The plant has a Level 1 treatment system. The plant is achieving a long-term average concentration for zinc of 1.9 mg/l. Data from Plant F118 were not used because Plant F118 is a multiproduct plant where process wastewater from all products is combined for common treatment, and the zinc chloride process wastewater comprises only five percent of the total flow to treatment, consequently, the effluent total zinc levels are lower than the levels achievable at a plant which produces zinc chloride only. Data from Plant F144 were not used for estimating the long-term average for total zinc because all of that long-term data is dissolved zinc. Variability factors for dissolved zinc developed at Plant F144, and presented in Appendix A, were used because the data from Plants F140 and F118 were not in a form that could be used to develop variability factors and there is no other data available. These are 2.0 for a 30-day average and 6.0 for a 24-hour maximum. From these values, limitations of 3.8 mg/l, 30-day average and 11.4 mg/l, 24-hour maximum, were derived. Use of variability factors derived from long-term TSS data at Plant F144 for total zinc is not appropriate because the TSS would account for the precipitated zinc hydroxide only, not the dissolved zinc. Total zinc is the sum of the precipitated and dissolved zinc.

Basis for BCT Effluent Limitations

On October 29, 1982, EPA proposed a new and revised methodology for determination of BCT for conventional pollutants. In this subcategory, only two conventional pollutants have been selected for limitation, pH and total suspended solids (TSS). Two tests are required according to the revised methodology, a POTW test and an industry cost effectiveness test. The POTW test is passed if the incremental cost per pound of conventional pollutant removed in going from BPT to BCT is less than $0.46 per pound in

TABLE 16-9. BPT EFFLUENT LIMITATIONS FOR ZINC CHLORIDE

Coventional Pollutants	Long-Term Avg. (mg/1)	VFR	Conc. Basis (mg/1)	
			30-day Avg.	24-hr. max.
pH	-	-	6-10*	6-10*
TSS	13.0(1)	1.9/3.3 (1)	25	43
Toxic Pollutants				
Arsenic	0.5(2)	2/6(3)	1.0	3.0
Zinc	1.9 (4)	2/6(3)	3.8	11.4
Lead	0.3(2)	2/6(3)	0.6	1.8

VFR - Variability Factor Ratio

* pH units
(1) Based upon long-term data at Plants F115, F125 and F140.
(2) Based upon Table 8-11.
(3) Based upon long-term data at Plant F144.
(4) Based upon long-term data at Plant F140.

1981 dollars. Under the proposed methodology, the industry test is passed if this same incremental cost per pound is less than 143 percent of the incremental cost per pound associated with achieving BPT.

The methodology for the first BCT cost test is as follows:

(1) Calculate the amount of additional TSS removed by the BCT technology.

(a) BPT long-term average = 13 mg/l
Level 2 long-term average * = 9.3 mg/l
*(See Sections 11 and 12 for derivation)

Difference = 3.7 mg/l

(b) Annual flow for model plant:

$(260\ m^3/day)(250\ day/yr) = 65{,}000\ m^3/yr$ "Small"
$(3785\ m^3/day)(365\ day/yr) = 1{,}381{,}525\ m^3/yr$ "Large"

(c) Total annual additional TSS removed for model plant:

Small Plant:

$(3.7\ mg/l)(65{,}000\ m^3/yr)(kg/10^6\ mg)(1000\ l/m^3)$
= 241 kg/yr
= 530 lbs/yr

Large Plant:

$(3.7\ mg/l)(1{,}381{,}525\ m^3/yr)(kg/10^6 mg)(1000\ l/m^3)$
= 5112 kg/yr
= 11269 lbs/yr

(2) Calculate the incremental cost, in dollars per pound of TSS removed, for the model plant.

(a) Incremental annualized cost for Level 2 technology, from Tables 16-6 and 16-7:

$29,000 "Small", and $71,400 "Large"

(b) Divide annualized cost by annual additional TSS removals:

($29,000 per yr) ÷ (530 lbs/yr) = $54.72 per lb of TSS removed for small model plant.

($71,400 per year) ÷ (11269 lbs/yr) = $6.34 per lb of TSS removed for the large model plant.

The costs for both model plants are far above the $0.46 per pound bench mark cost. Therefore, the candidate BCT technology failed the first BCT cost test there is no need to apply the second BCT cost test.

On October 29, 1982, EPA proposed a revised BCT methodology. While EPA is considering revising that methodology, we have determined that in this subcategory no technology beyond BPT will pass the proposed BCT cost test or any other BCT test that the Agency is likely to adopt. Accordingly, in this subcategory we are setting BCT equal to BPT. As a result, BCT for TSS is equal to the BPT limitations. However, the Agency will need to reconsider the BCT limitations for this subcategory when a new BCT cost test is promulgated.

Basis for BAT Effluent Limitations

Application of Advanced Level Treatment

Utilizing the cost estimates in this report, the Agency has analyzed the cost of the base level systems (BPT - Level 1) and an additional advanced level option for toxic pollutant removal. The economic impacts on the Zinc Chloride Subcategory have been evaluated in detail and taken into consideration in the determination of the BAT regulations.

For BAT, the Agency is promulgating limitations based on treatment consisting of Level 1 plus Level 2 technology. Toxic pollutants limited by the promulgated BAT regulation are arsenic, lead, and zinc.

A. Technology Basis

Alkaline precipitation followed by clarification, dewatering of the sludge in a filter press, and filtration of the clarifier effluent form the selected BAT technology basis.

B. Flow Basis

The limitations have been developed on a concentration basis only.

C. Selection of Pollutants to be Regulated

Toxic Pollutants

The toxic pollutants arsenic, lead, and zinc have been selected for BAT limitation. Table 16-10 presents the BAT limitations for the Zinc Chloride Subcategory.

D. Basis of BAT Pollutant Limitations

As in BPT, the BAT limitations are presented as concentrations (mg/l).

Toxic Pollutants

a. Arsenic

Because there is no long-term monitoring data for arsenic, the BAT limitations for arsenic are based on estimated long-term averages achievable with Level 2 treatment taken from Table 8-11, and variability factors computed from long-term data for dissolved zinc at Plant F144 presented in Appendix A for the reasons given below for zinc. Using a value of 0.5 mg/l as a long-term average, 2.0 as a variability factor for 30-day average concentrations, and 6.0 as a variability factor for 24- hour maximum computations, concentration limits of 1.0 mg/l (30-day average) and 3.0 mg/l (24-hour maximum) are obtained.

b. Lead

The BAT limitations for lead are based on long-term data from Plant F144. These data indicate a long-term average effluent lead concentration of 0.038 mg/l. Variability factors at Plant F144 were used. These are 1.25 for a 30-day average and 4.8 for a 24-hour maximum. From these values, limitations of 0.048 mg/l, 30-day average, and 0.18 mg/l, 24-hour maximum were derived.

c. Zinc

The BAT limitations for zinc are based upon removals of greater than 80% of total zinc present from the effluent of a BPT-type treatment system as demonstrated by a treatability study of filtration at Plant F144. A long-term average effluent zinc concentration of 0.38 mg/l represents 80% removal of total zinc from the BPT long term average value of 1.9 mg/l. Filtration technology is applicable for removal of solids including precipitated metal hydroxides such as zinc hydroxide but has little effect on removing dissolved

TABLE 16-10. BAT EFFLUENT LIMITATIONS FOR ZINC CHLORIDE

Toxic Pollutants	Long-Term Avg. (mg/l)	VFR	Conc Basis (mg/l) 30-day avg.	Conc Basis (mg/l) 24-hr. max.
Arsenic	0.5(1)	2/6(3)	1.0	3.0
Zinc	0.38(2)	2/6(3)	0.76	2.28
Lead	0.038(3)	1.25/4.79(3)	0.048	0.18

VFR - Variability Factor Ratio

(1) Based upon Table 8-11.
(2) Based upon 80 percent removal demonstrated by Plant F144 treatability study.
(3) Based upon long term data at Plant F144.

metals. The total zinc discharged from the filter is the sum of the dissolved zinc and precipitated zinc that passes through the filter. Because our treatability study demonstrated that filtration is very effective in removing precipitated zinc, the total zinc discharged consists mostly of dissolved zinc. Therefore, use of dissolved zinc data to estimate variability factors is appropriate in the absence of any long-term data from a zinc chloride plant with Level 2 technology. Variability factors developed for dissolved zinc at Plant F144, and presented in Appendix A, were used. These are 2.0 for a 30-day average and 6.0 for a 24-hour maximum. From these values, limitations of 0.76, 30-day average, and 2.3 mg/l, 24-hour maximum, are obtained.

Basis for NSPS Effluent Limitations

For NSPS, the Agency is promulgating limitations based on the BAT technology since no additional technology which removes significant additional quantities of pollutants is known. The pollutants limited include pH, TSS, arsenic, lead, and zinc. The NSPS effluent limitations are listed in Table 16-11.

The limitations for arsenic, lead, and zinc are the same as for BAT. See the BAT section above (pages 407 and 409) for the development of those limitations. The pH limitations are within the range 6-10, as described above for BPT (pages 401-403). The TSS limitations are based on filtration and are developed as follows:

> Since no long-term monitoring data for TSS is available from any zinc chloride plant with Level 2 treatment, the NSPS limitations for TSS are based on an average of long-term TSS monitoring data from Plants A and K as presented in Appendix A of the Phase I Development Document which uses the same Level 2 (filtration) technology to control TSS that is promulgated for the zinc chloride subcategory. A long-term average of 9.3 mg/l (the average of both plants) was used to develop the discharge limitations for plants employing filtration. Variability factors, also obtained from Plants A and K, of 1.8 for a monthly average and 3.0 for a 24 hour maximum were used yielding TSS concentration limits of 17 mg/l and 28 mg/l respectively.
>
> The treatability study (pages 385-387 above) showed higher TSS removals than are required by the NSPS. However, the treatability study was only a three day test, which must be considered less reliable than long-term data from operating

TABLE 16-11. NSPS EFFLUENT LIMITATIONS FOR ZINC CHLORIDE

Conventional Pollutants	Long-Term Avg.(mg/l)	VFR	Conc Basis (mg/l)	
			30-day avg.	24-hr. max.
TSS	9.3(1)	1.2/3.0	17	28
Toxic Pollutants				
Arsenic	0.5(2)	2/6(3)	1.0	3.0
Zinc	0.38(3)	2/6(3)	0.76	2.28
Lead	0.038(4)	1.25/4.79(4)	0.048	0.18

VFR - Variability Factor Ratio

(1) See Text
(2) Based upon Table 8-11
(3) Based upon 80 percent removal demonstrated by Plant F144 treatability study
(4) Based upon long term data at Plant F144

facilities. Therefore, the treatability study was not relied upon to establish TSS limitations for NSPS.

Basis for Pretreatment Standards

Existing Sources

The Agency is promulgating PSES equal to BAT limitations because BAT provides better removal of arsenic, lead, and zinc than is achieved by a POTW and, therefore, these toxic pollutants would pass through a POTW in the absence of pretreatment. Pollutants regulated under PSES are arsenic, lead, and zinc. Table 16-9 contains these limitations.

Using the summary data presented in Tables 16-6 and 16-10, the Agency has estimated that percent removals for arsenic, lead, and zinc by comparing the untreated waste concentrations for those three metals with the concentrations of those same three pollutants in effluent from the selected BAT technology. The calculations are as follows:

Arsenic: Raw Waste = 2.8 mg/l
BAT = 0.5 mg/l

Percent Removal = [(2.8 - 0.5) ÷ (2.8)](100)
= 82%

Lead: Raw Waste = 0.86 mg/l
BAT = 0.038 mg/l

Percent Removal = [(0.86 - 0.038)/(0.86)](100)
= 96%

Zinc: Raw Waste = 150 mg/l
BAT = 0.38 mg/l

Percent Removal = [(150 - 0.38)/(150)] (100)
= 99.75%

The percent removals are greater than the removals for lead (48%) and zinc (65%) achieved by 25% of the POTWs in the "50 Cities" study (Fate of Priority Pollutants in Publicly Owned Treatment Works, Final Report, EPA 440/1-82/303, September , 1982). Only limited data is available on removal of arsenic by POTWs, but the removals for other toxic metals by 25% of the POTWs in that study ranged from 19% to 65%. We assume that the POTW removals of arsenic are in that range. Therefore, since the BAT technology achieves a greater percent removal of arsenic, lead, and zinc than is achieved by a well operated POTW with secondary treatment, those three toxic metals would pass-through the POTW in the absence of pretreatment.

Using the summary data presented in Tables 16-9 and 16-10, the Agency has also estimated the percent removals for lead and zinc by comparing the concentrations of those two toxic metals in effluent from BAT treatment with the concentrations of the same two pollutants in effluent from BPT treatment. Since the concentrations of arsenic are the same from BPT and BAT technology, the Agency compared the untreated waste concentrations for arsenic with the effluent concentration from BAT treatment for that metal. The calculations are as follows:

Arsenic: Raw Waste = 2.8 mg/l
BAT = 0.5 mg/l

Percent Removal = [(2.8 - 0.5) ÷ (2.8)](100)
= 82%

Lead: BPT = 0.3 mg/l
BAT = 0.035 mg/l

Percent Removal = [(0.3 - 0.038) ÷ (0.3)] (100)
= 87%

Zinc: BPT = 1.9 mg/l
BAT = 0.38 mg/l

Percent Removal = [(19 - 0.38) ÷ (1.9)[(100)
= 80%

The percent removals are greater than the removals for lead (48%) and zinc (65%) achieved by 25% of the POTWs in the "50 Cities" Study.

Only limited data is available on the removal of arsenic, but removals achieved by 25% of the POTW's in that study for other toxic metals ranged from 19% to 66%. We assume that the POTW arsenic removals are in that range. Therefore, since the BAT technology achieves a greater percent removal of arsenic, lead, and zinc than is achieved by a well operated POTW with secondary treatment, those three toxic metals would pass-through the POTW in the absence of pretreatment.

New Sources

The Agency is promulgating PSNS equal to NSPS for toxic pollutants. The pollutants limited include arsenic, lead, and zinc and are listed in Table 16-9.

SECTION 16 REFERENCES

1. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and Standards for the Inorganic Chemicals Manufacturing Point Source Category," EPA Report No. 440/1-79-007, June 1980.

2. JRB Associates, Inc., "An Assessment of pH Control of Process Waters in Selected Plants," Draft Report to the Office of Water Programs, U.S. Environmental Protection Agency, 1979.

SECTION 17

BAT REVISIONS

BACKGROUND

The effluent limitations guidelines and standards for the sodium chloride (solution brine-mining process), calcium chloride, and sodium sulfite subcategories were promulgated on March 12, 1974 and are still in effect. These guidelines set numerical discharge limitations for BPT and established BAT limitations, NSPS, and PSNS of no discharge of process wastewater pollutants. PSES were reserved for each subcategory. The technology used as a basis for the BAT limitations, NSPS and PSNS for the sodium chloride (solution brine-mining process) and calcium chloride subcategories was the use of surface condensers instead of barometric condensers. For the sodium sulfite subcategory, the technology basis was evaporation of the treated wastewater.

Each of these subcategories was excluded from further national BAT regulation development under the provisions of Paragraph 8(a)(i) of the Settlement Agreement in the Phase I Inorganic Chemicals BAT regulation (47 FR 28260, June 29, 1982), because there was an existing zero discharge BAT. Each of these subcategories was included in the Phase II Inorganic Chemicals regulation development study to consider appropriate PSES, because PSES for these subcategories were not included in the March 1974 promulgation (see Section 18).

On May 19, 1981, the Salt Institute petitioned the Agency to review the BAT limitations for the sodium chloride (solution brine-mining process) subcategory because the industry believed the costs of compliance with the zero discharge requirements, including the adverse effect on production efficiency that would result from the use of surface condensers rather than barometric condensers, were not justified by the effluent reductions to be achieved.

After receiving the petition from the sodium chloride industry to reconsider the BAT guidelines for sodium chloride, the Agency extended its study to include the calcium chloride and sodium sulfite subcategories because they are also subject to a zero discharge of process water requirement for BAT but are allowed a discharge under BPT.

EPA is amending existing BAT limitations for facilities engaged in production of sodium chloride (solution brine-mining process) and sodium sulfite. No changes are promulgated for the calcium chloride subcategory. The remainder of this section sets forth the background, rationale for the amendments, and recommendations concerning each subcategory.

SODIUM CHLORIDE (Solution Brine-Mining Process)

General

In early 1984, the sodium chloride (solution brine-mining process) subcategory included 18 plants (1), none of which are indirect dischargers. The annual production was estimated at about 3,175,000 metric tons (3,500,000 short tons) per year in 1981 (3.36 million metric tons in 1979). The estimated daily discharge is 15,503 m^3/day (4.1 million gallons per day) of barometric condensate wastewater.[1] The plants are located in inland rural areas where the annual precipitation is too high to permit solar evaporation of the water from the brine to be used to recover the sodium chloride product. Fourteen of the existing eighteen plants operating in early 1984 discharge their wastewater (barametric condenser water) directly. Two of the eighteen plants achieve zero discharge by reinjection (both also use cooling ponds). Two plants employ cooling towers with one achieving zero discharge, and the second only discharges infrequently during cooling tower blowdown. Hence, there are fifteen dischargers in the subcategory. It should be noted that the 1974 rulemaking considered only the handling of condensate alone rather than total flow of condensate plus cooling water (see note below).

Process Description

In the production of sodium chloride by the solution brine-mining process, underground salt deposits are mined by pumping water into the salt deposit where the water dissolves the salt and forms a concentrated solution or brine. The brine is then pumped back to the surface where it is chemically treated to remove impurities and then evaporated to recover the sodium chloride (table salt). The chemical treatment varies from plant to plant, but a typical process will first aerate the brine to remove dissolved hydrogen sulfide and oxidize any iron salts present to the ferric state. The brine is then treated with soda ash and caustic soda to convert most of the calcium, magnesium, iron, and other metal impurities present to insoluble precipitates (as hydroxides or carbonates) which are removed by clarification. The brine is then evaporated using multiple-effect evaporators. As the water is removed, the salt crystals form and are removed as a slurry. The solids are screened to remove lumps, washed with fresh brine to remove calcium sulfate crystals (which are returned to the evaporator), filtered, dried, and screened.

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[1] This amount represents only the actual amount of condensate before mixture with contact cooling water in the barometric condenser. The actual total amount of discharged process water (condensate plus cooling water) is estimated to be 925,000 m^3/day (244 MGD).

Water Use and Wastewater Characteristics

The process wastewater discharged consists essentially of the barometric condenser water used to condense the steam and maintain a vacuum in the multiple-effect evaporators. As the water bubbles, boils, and evaporates, some salt crystals are carried over in the escaping vapor (become entrained) and are mixed with the barometric condenser water and subsequently discharged. Any impurities, such as toxic pollutants, that may be present in the evaporating solution, could also become entrained and contaminate the barometric condenser wastewater. The order of concentration of contaminants in the wastewater, from highest to lowest, will be the same as the order of their concentrations in the evaporating solution. The residue after evaporation is the product sold. Accordingly, the most likely contaminant in the barometric condenser wastewater is the product itself.

The technology used as a model for the zero discharge BAT promulgated in 1974 assumed replacement of barometric condensers by surface condensers (e.g., shell and tube condensers). The surface condensers would prevent contact of the condensed vapor and entrained solids with the cooling water which is subsequently discharged, and consequently reduce the volume of the condensate to a level that allows the recycle of the complete wastewater stream as make-up water for the process (e.g., pumped back to the mine for solution mining) thereby eliminating the need to discharge process water. Presently, the barometric condensers currently installed bring large amounts of cooling water in contact with condensate from the last evaporator, and even though current data demonstrates that entrainment of process water pollutants is low, this stream is considered to be process water by definition. In response to the petition from the Salt Institute, we have reexamined the installed cost and pollutant reduction associated with the use of surface condensers using information that was not available in 1974.

Review of Available Data

Most of the data available have been previously published by EPA, and all of it was acquired during the course of studies conducted to assist in developing effluent guidelines for the Inorganic Chemicals industry. Data specific to the sodium chloride (solution brine-mining process) industry are contained in the "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganics Products segment of the Inorganic Chemicals Manufacturing Point Source Category," EPA-440/1-74-007a (March, 1974) (2). Additional data have been collected and developed during the Phase I and Phase II studies which directly bear on the issue of pollutant entrainment. These data include the analytical data on barometric condenser discharge water from two sodium chloride facilities as well as several plants from other industries.

In the sodium chloride (solution brine-mining) manufacturing process, the source of the wastewater is barometric condenser wastewater. Accordingly, we also reviewed data for similar processes in other inorganic chemicals industries. Relevant data are available for the chlor-alkali (diaphragm cell), sodium thiosulfate, sodium chlorate, and ammonium bromide subcategories. The chlor-alkali (diaphragm cell) data are contained in the "Development Document for Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Inorganic Chemicals Manufacturing Point Source Category" EPA 440/1-82/007 (July, 1982) (3). The data for the sodium thiosulfate and ammonium bromide subcategories includes both screening and verification data acquired in 1978 (sodium thiosulfate) and 1980 (ammonium bromide) and data submitted to EPA in 1976 and 1980, respectively, in response to our requests for data under Section 308 of the Act. The data for the sodium chlorate subcategory were developed under Phase II and are summarized elsewhere in this document (Section 15 and Appendix A). The 1974 data included results of analyses for only a few metals; the more recent data included results of analyses for all toxic metal and toxic organic pollutants. In all cases, the products are being recovered from solution by evaporating the water and condensing the escaping steam using barometric condensers. Also, in all cases, the existence of toxic organic pollutants is highly unlikely because organic substances are neither used in the production process nor likely contaminants of the raw materials. In any event, no toxic organic pollutants are likely to be added to wastewater as the result of the NaCl process because the process raw material is salt (formed millions of years ago) and no organic chemicals are added in the process. Essentially then, we have a purely inorganic process in the case of sodium chloride produced in the manner described previously.

The data acquired in 1973 for barometric condenser water from sodium chloride production are presented in the following table (from Table 22, page 143 of the 1974 Development Document, Reference 2):

			Concentration (mg/l)			
Stream	TSS	pH	Ca	Cl	SO_4	Fe
Intake	0	8.0	128	65	13	0.24
Effluent	0	8.1	147	120	37	0.23

These data show that the barometric condenser discharge contains some net addition of calcium, sulfate, and chloride, but essentially no iron. The sodium chloride addition to the discharge averages 2 pounds per ton of product or 0.1 percent (page 141 of the 1974 Development Document, Reference 2). The calcium and sulfate carried over are from the small amount left after purification of the brine. The absence of any net increase in iron (Fe) indicates that no toxic metals are carried over either, because the iron is present in the treated brine at higher concentrations than any of the toxic metals. Treatment of the brine to remove iron by precipitation as the hydroxide or carbonate will also reduce the amount of toxic metals as has been demonstrated throughout the inorganic chemicals and other industries. Precipitation of toxic metals (and iron) as the metal hydroxide is the technology basis for the promulgated BPT limitations for most of the subcategories of the Inorganic Chemicals Manufacturing industry. This treatment generally reduces toxic metal concentrations to less than 1 milligram per liter and iron concentrations to less than 10 ppm (see the Development Document for the Inorganic Chemicals Effluent Guidelines and Standards, EPA 440/1-82/007, July, 1982, Tables 14-17, 14-18, 14-33b, 14-34, and 14-37, Reference 3). Because the toxic metal, iron, sodium and calcium compounds in the purified brine do not evaporate with the boiling water, the only way these substances can enter the barometric condenser wastewater is by entrainment. The most likely substance to be entrained is the substance present in the purified brine in the greatest amount, which is the sodium chloride product. Of toxic metals and iron, the most likely pollutant to be entrained is the iron since the treated brine contains more iron than any of the toxic metals. The data above show that the discharge contains less than 60 ppm chloride (a measure of the amount of sodium chloride entrained) and no net addition of iron. Treatment of the brine produces a product that is 99.8 percent pure sodium chloride, and the data above indicate that much of the impurities are calcium and sodium sulfates and calcium chloride.

TABLE 17-1. TOXIC METAL DISCHARGES IN BAROMETRIC CONDENSER WASTEWATER

	Concentration (ug/l(ppb))(1) Plant						
Pollutant	A	B	C	D	E	F	G
Sb	<20	<20	<20	<20	<10	<10	<2
As	<10	<10	<10	28	<3	8	<2
Be	<15	<15	<15	<15	<0.2	0.7	<2
Cd	<2	<25	<2	<2	0.3	1.1	24
Cr	<50	<50	<50	<50	6.5	18	22
Cu	<50	<50	<50	<50	6.5	28	3
Pb	<10	<10	<12	<10	5	13	2
Hg	18	<0.4	<0.4	<0.4	10	1.6	<3
Ni	<50	<50	<50	65	5	10	<5
Se	<10	<50	<10	<10	<9	<9	4
Ag	<15	<15	<15	<15	20	0.9	49
Tl	<20	<2	<2	<2	<2	5	33
Zn	30	<75	<50	135	<50	270	25

< = less than

Plants A to E = Chlor-Alkali (Diaphragm Cell)

Plant F = Sodium Thiosulfate

Plant G = Ammonium Bromide

(1) All values are maximum daily values observed from three 24-hour composite samples obtained during verification sampling at Plants B, C, D, and G. Values reported for Plants A, E, and F are the values observed during screen sampling (72-hour composites).

The conclusion to be drawn from the data described above is that the barometric condenser water discharged from plants in the solution brine-mining process for sodium chloride production does not contain toxic metals at significant levels.

The toxic metal discharges in barometric condenser wastewater for the chlor-alkali (diaphragm cell), (Plants A-E), sodium thiosulfate (Plant F), and ammonium bromide (Plant G) subcategories are shown in Table 17-1.

As shown in Table 17-1, none of the toxic metals are present at significant levels and most metals are below the detectable level. In contrast, the maximum concentrations of toxic metals in the solutions being evaporated were as follows (samples taken at the same time as those in Table 17-1):

		Concentration (ug/l (ppb))			
Plant	Cu	Cr	Pb	Ni	Zn
A	1,700	1,900	2,000	22,000	1,600
B,C,D	600	-	160	-	500
E	530	940	260	-	240
F	-	260	-	-	550
G	140	-	220	-	650

The sampling data above strongly support the conclusions that the toxic metals are left behind in the evaporating solution, and that discharges of barometric condenser wastewater do not contain significant levels of toxic metals.

Additional relevant data are available from an ammonium bromide plant, with a total of 18 months of monitoring data for ammonia concentrations in the condenser discharge as well as three-day screening and verification sampling results. The long term average ammonia discharge is 1.4 mg/l ammonia, with a maximum ammonia concentration of 5.6 mg/l. This shows practically no carry-over (entrainment) of the ammonium bromide salt. The average screening and verification results for ammonia and bromide are as follows (in mg/l):

Ammonia	3.2 mg/l	Bromide	6.0 mg/l

In this case, the ammonium bromide is the product, and would be expected to be found at higher concentrations in the wastewater than any other pollutant. The fact that the ammonia and bromide are at very low levels shows that there is very little carryover of the product, and hence negligible amounts of toxic pollutants would be expected in barometric condenser wastewater.

TABLE 17-2. CHEMICAL COMPOSITION OF BAROMETRIC CONDENSATE FROM PLANT F122 (ALL VALUES ARE AVERAGE OF THREE DAILY MEASUREMENTS).

Pollutant	Barometric Condensate
Sb	<0.007
As	<0.002
Be	<0.0002
Cd	<0.0037
Cr	0.22*
Cu	0.022
Pb	<0.0016
Hg	<0.0013
Ni	2.87**
Se	<0.007
Ag	0.00027
Tl	<0.003
Zn	<0.0025

*Added to the process as sodium dichromate.

**Evaporators are made of a nickel alloy.

Another example which is relevant is one from the sodium chlorate subcategory at Plant F122. This plant was described in detail in Section 15. Table 17-2 presents data on the toxic metal content of the barometric condenser water at Plant F122. Each entry is an average of three daily values obtained during screening and verification sampling.

These data confirm that the metals concentrations attributable to comparable portions of the process are extremely low levels. Chromium present in these streams is explained by the addition of sodium dichromate in the process used for sodium chlorate. Nickel is present because stainless steel is used in the evaporators.

Our conclusion from this data review is that discharges of barometric condenser wastewater from production of sodium chloride by the solution brine-mining process do not contain significant levels of toxic pollutants.

This conclusion is confirmed by analytical data submitted by two sodium chloride (solution brine-mining process) plants to the permitting authorities as part of the applications for NPDES permits for those plants. That data shows all toxic metal pollutants are below significant levels, and most are below the detection limit.

Treatment Cost Estimates

In order to determine the potential costs of installation of surface condensers in the sodium chloride subcategory (solution brine-mining process), a model plant was chosen and the costs of installation of surface condensers were estimated based upon its characteristics.

The hypothetical model plant chosen produces 1088.4 metric tons per day (1200 short tons) of purified sodium chloride. This size model plant was chosen because it is similar to that used in the 1974 Development Document. Therefore costs and flows are comparable. Average daily process water flow (condensate plus contact cooling water in the barometric condenser) at this plant is taken as 45,420 m^3/day (12 MGD) of which 757 m^3/day (0.2 MGD) is condensate from the last evaporation stage. In this case, there is a 60-fold dilution of the final condensate before discharge.

The following assumptions were utilized in developing the cost estimates presented in Table 17-3.

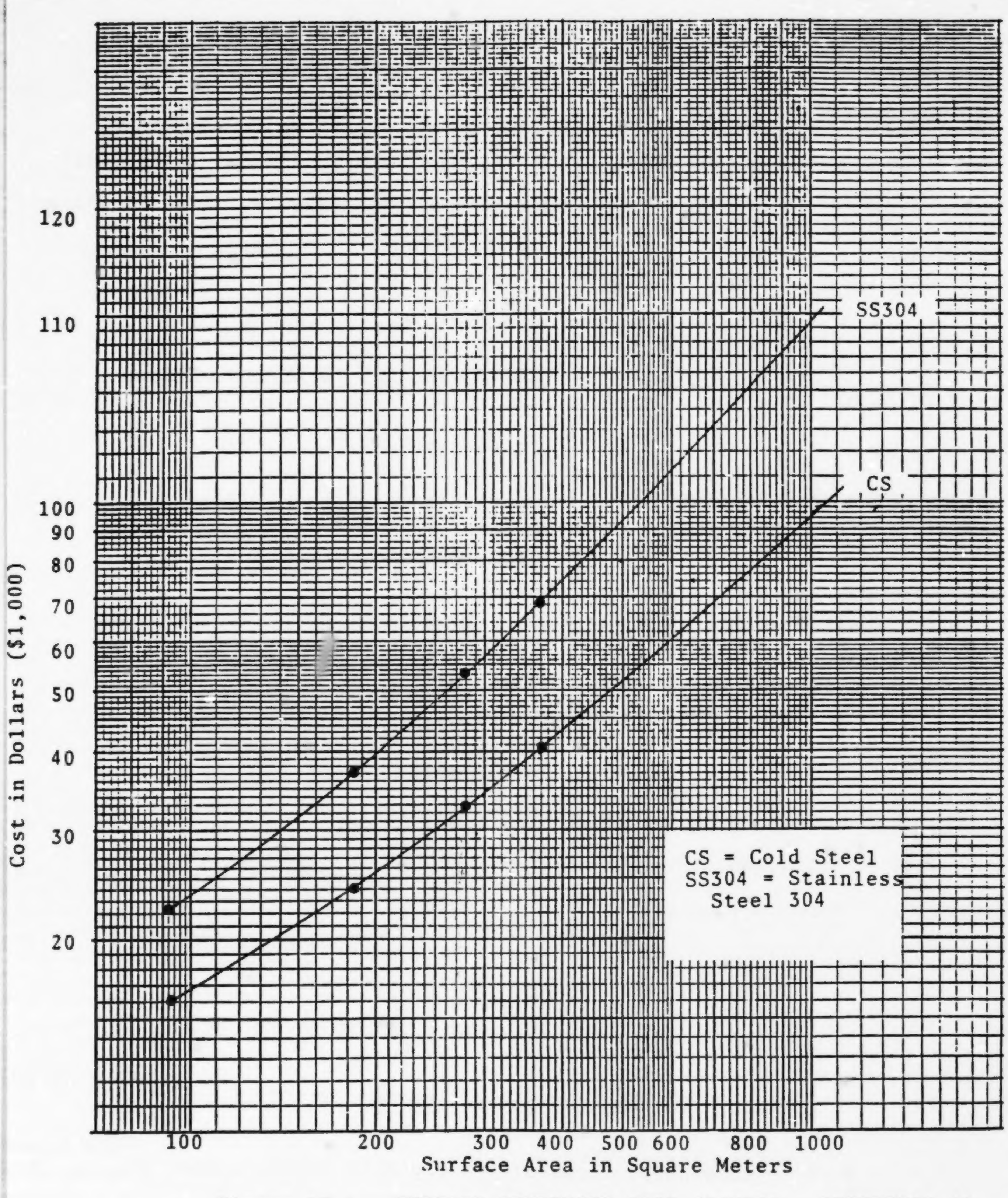

Figure 17.1. SURFACE CONDENSER COST (SOURCE: REFERENCE 4).

TABLE 17-3. WATER EFFLUENT TREATMENT COSTS AND RESULTING WASTE-LOAD CHARACTERISTICS FOR MODEL PLANT

SUBCATEGORY: Sodium Chloride

ANNUAL PRODUCTION: 397,266 METRIC TONS (438,000 short tons)

DAILY FLOW: 45,420 CUBIC METERS (total flow); 757 m^3 condensat

PLANT AGE: N/A YEARS PLANT LOCATION: N/A

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1A	1B	2	3	4
Facilities	30.0	150.0			
Installed Equipment (Including Instrumentation)	172.3	861.3			
Engineering	40.5	202.3			
Contractor Overhead and Profit	36.4	182.6			
Contingency	27.9	139.6			
Land	-	-			
Total Invested Capital	307.1	1,535.2			
Annual Capital Recovery	50.0	249.8			
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	58.2	245.2			
Residual Waste Disposal	-	-			
Total Annual Cost	108.2	495.0			

b. RESULTING WASTE-LOAD CHARACTERISTICS

Pollutant	Avg. Conc. Untreated (mg/l)	Long-Term Avg. Concentration (mg/l) After Treatment To Level 1A	1B	2	3	4
TSS	27	0	0			

c. TREATMENT DESCRIPTION

LEVEL 1A: Surface condenser - loss of 10% capacity during summer months

LEVEL 1B: Surface condenser - no loss of capacity

The surface condenser would replace the existing barometric condenser. The costs developed here do not take into account the dismantling of the barometric condenser, the possible reuse of equipment or parts, or any salvage value. No estimate of costs associated with loss of production occurring while the installation of the surface condensers is proceeding has been utilized in preparation of these estimates.

Costs are shown for two systems. The Level 1A condenser is the smaller of the two. Its use will result in a potential loss of production during the summer months when the temperature of the incoming cooling water is assumed to be about 25°C (77°F). This loss of capacity is approximately 10 percent.[2] The Level 1B condenser is sized such that there would be no loss in productivity during such a period. In both cases, the amount of condensate to be handled was assumed to be the same.

In both cases, a building is provided for the housing of the condensers.

Facilities	Level 1A	Level 1B
Building	85 m^2	5 - 85 m^2
Equipment		
Surface Condenser (cold steel) (See Figure 17-1)	920 m^2	5 - 920 m^2
Operating Personnel	2 m.h./day	5 m.h./day

Level 1B condensers are 5 times the size of the level 1A condensers.

Since the available information indicates that the model plant is a typical plant for the industry, it is estimated that replacement of barometric condensers with surface condensers at all 15 dischargers would require a total capital and annual investment as follows (1982 dollars):

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[2] If the temperature of the incoming cooling water is greater than 25°C (77°F), a greater loss of capacity would result.

	Level 1A	Level 1B*
Total Capital Costs	$4,606,500	$23,028,000
Total Annual Costs	$1,623,000	$ 7,425,000

* Sized for no loss of capacity during summer months

The level 1A costs do not include the costs associated with the loss of 10% of the production capacity. Because available data lead to the conclusion that the barometric condenser wastewater in this subcategory does not contain toxic pollutants at significant levels, the Agency does not believe these costs are justified. Therefore, we are withdrawing the currently effective BAT regulation for this subcategory.

We are also excluding the subcategory from further national BAT and PSES regulation development because based on the available data it is concluded that the wastewater does not contain toxic or nonconventional pollutants at significant levels and because there are no indirect dischargers in this subcategory.

New Source Performance Standards

We proposed to retain the zero discharge regulation for NSPS on the basis that noncontact condensers were not significantly more expensive for a new plant to install than contact condensers. However, industry comments estimated that noncontact condensers cost about three times as much as contact condensers. We have reanalyzed the condenser costs. We also identified three existing plants which achieve zero discharge with contact condensers and recycle of the cooling water through cooling towers or cooling ponds. We estimated the additional cost for new plants to use cooling towers or cooling ponds and contact condensers. The new cost estimates were developed as given below.

The design and sizing of facilities and equipment for these wastewater treatment options are very sensitive to local climatic and operating conditions. The costs presented below are estimates based on the postulated assumptions. The accuracy of these estimates is thought to be ± 25% for the set of assumptions stated here. Actual costs incurred at any one plant could vary significantly from the values presented depending especially upon climatic conditions and land costs.

Cooling Pond

Costs of cooling ponds by which zero discharge is achieved are based on the following assumptions:

Daily Flow	45,420 m^3 (12 MGD)
Avg. Daily Temp.	20°C (68°F)
Rel. Humidity	50%
Solar Radiation Input	315 Watts/m^2 (100 BTU/hr/ft^2)
Equilibrium Temp.	27°C (80 F)*
Receiving Temp.	30°C (86°F)*
Returning Temp.	28°C (83°F)*

*Assumed conditions are probably representative of conditions in Michigan.

This yields approximately a 5 hectare (12.3 acre) cooling pond. The costs presented below are for a somewhat larger 8 hectare (20 acre) cooling pond. In addition, included in the costs are 400 m (1300 ft) of piping and pumps to return the cooled water to the plant.

With respect to land costs, a cost of $12,000/acre was assumed. However, land costs may actually be closer to $1,000-2,000/acre in some rural areas. In addition, costs presented below assume a 20 acre area. A 12.3 acre area may be adequate in most instances. Tables 1 and 2 are summaries of capital and operating costs for the cooling pond option.

Table 1. Capital and Annual Costs for the Cooling Pond NSPS Option.

Capital Costs	
Facilities	
Cooling Pond	$109,600
Piping	55,100
Equipment	
Pumps	44,800
Installation	42,900
Engineering	50,500
Contractor OH&P	45,400
Contingency	34,800

Land		240,000*	(may vary from $12,300-240,000)
	Total	$623,100	($395,400 to $623,100)

Annual Costs

Operations and Maintenance		
Operating Personnel		$ 18,300
Facility & Equipment Maintenance		38,300
Materials		---
Energy		47,900
Monitoring and Analysis		**
Taxes and Insurance		18,700
Residual Waste		---
Amortization		62,300
	Total	$185,500

*See text
**Zero discharge system

Cooling Tower

The cooling tower costs are based on the following assumptions:

Daily Flow	45,420 m^3 (12 MGD)
Wet Bulb Temp.	25°C (78°F)
Receiving Temp.	30°C (86°F)
Returning Temp.	28°C (83°F)
Fan Horsepower	120 HP

Additionally included in the costs are a holding pond sized for six hours retention of wastewater, 150 meters of piping and pumps. Tables 3 and 4 are summaries of the capital and annual costs associated with this option.

Table 2. Capital and Annual Costs for the Cooling Tower NSPS Option.

Capital Costs

Facilities	
Holding Pond	$ 22,800
Piping	20,700
Equipment	
Cooling Tower	187,500
Pumps	44,800
Installation	222,400
Engineering	99,600
Contractor OH&P	74,700
Contingency	57,300
Land	27,000
Total	$657,200

Annual Costs

Operations and Maintenance	
Operating Personnel	$ 27,400
Facility and Equipment Maintenance	63,000
Materials (Water Trmt. Chem.)	7,000
Energy	105,400
Monitoring and Analysis	---
Taxes and Insurance	19,700
Residual Waste	---
Amortization	102,500
Total	$325,000

The economic impact analysis shows that the zero discharge NSPS, whether achieved using noncontact condensors or contact condensors with recycle of cooling water, is not a barrier to entry. The economic impact analysis included the assumption that industry's figures were correct. Since there is no barrier to entry, there is no need to change the currently effective NSPS or PSNS for this subcategory.

Basis for BCT Effluent Limitations

On October 29, 1982 EPA proposed a new and revised methodology for determination of BCT for conventional pollutants (47 FR 49176). The methodology has been described in detail in several preceding sections of this document (see, for example, Section 16 - "Basis for BCT Effluent Limitations").

Two candidate BCT technologies have been tested in this subcategory, namely, the use of surface condensers in place of barometric condensers to eliminate the discharge of total suspended solids (TSS), and the use of filters to reduce the discharge of TSS (TSS is the only conventional pollutant in the wastewater).

A. Option 1 - Surface Condensers

The use of surface condensers at the 15 discharging plants is estimated to be capable of removing approximately 450,000 kg (992,000 lb) of TSS annually at a cost of $1,623,000 (for the Level 1A, or smaller condenser). The annual cost for the industry using the larger condenser with no loss of capacity would be $7,425,000. Therefore, the computation of TSS removed would be as follows:

(BPT limitation) (ann. production) = TSS removed/yr.

(0.17 kg/kkg) (2,645,833 kkg/yr) = 449,792 kg/yr

For the surface condenser option as BCT:

$$\frac{\$1,623,000/\text{yr}}{449,792\ \text{kg/yr}} = \$3.61/\text{kg}\ (1\ \text{kg} = 2.2\ \text{lbs.})$$

$$= \$1.64/\text{lb. TSS removed (1982)}$$

As a result of the above computation, the candidate BCT technology failed the BCT - POTW cost test. Since the Level 1A option failed the BCT cost test, inclusion of costs due to loss of production and production capacity, or applying the BCT cost-test to the more expensive Level 1B would also fail the test because the amount of TSS removed would not change with these more expensive options. Use of cooling ponds or cooling towers are also more expensive than the Level 1A option (See above, NSPS), and would also fail the proposed BCT cost test.

B. Option 2 - Granular Media Filtration

The use of granular media filtration at the 15 discharging plants is estimated to be capable of removing 240,000 kg (525,000 lb.) of additional TSS (over BPT) annually at a cost of $3,750,000. The TSS removals were estimated by assuming the filter would remove 50% of the TSS. This removal is better than that normally expected from a filter, and tends to minimize the cost per pound of TSS removed. The cost of the filter has been estimated using the cost tables in Chapter 10.

(Additional TSS removed) (Ann. prod.) = Add. TSS removed/yr.
(0.09 kg/kkg) (2,645,833 kkg/yr) = 240,000 kg/yr.

For the granular media filtration option as BCT:

$$\frac{\$3,750,000/\text{yr}}{240,000\ \text{kg/yr}} = \$15.63/\text{kg}\ (1\ \text{kg} = 2.2\ \text{lbs.})$$

$$= \$7.10/\text{lb. TSS removed (1982)}$$

As a result of the above computations, the candidate BCT technology failed the BCT-POTW test ($0.43 per pound (1982)).

All technologies to control conventional pollutants more stringent than BPT failed the proposed BCT cost test. However, EPA is considering revising that proposed methodology. In this subcategory, it is not clear that all technologies to control conventional pollutants more stringent than BPT would fail a revised BCT cost test. Therefore, the Agency is deferring establishing a BCT for the sodium chloride (solution brine-mining process) subcategory.

CALCIUM CHLORIDE (Brine Extraction Process)

General

The calcium chloride subcategory (brine extraction process) includes seven plants, none of which are indirect dischargers. Three of these facilities are known to achieve zero discharge by reinjection of the brine, and none of the seven have a process water discharge. Four plants are located in desert areas of California, and three are located in Michigan. All seven use natural brines as raw material. The annual production capacity of calcium chloride from all processes is 1,047,585 metric tons (1,155,00 short tons) per year(5). The U.S. Bureau of Mines reported actual total production of 735,700 metric tons (811,135 short tons) in 1980, however, 526,978 metric tons (581,012 short tons) or 71.6 percent were produced from natural sources (brines) (6).

The uses of calcium chloride are principally for deicing (30 percent), dust control (25 percent), industrial uses (20 percent), oil recovery (10 percent), concrete set-accelerator (5 percent), tire ballasting (3 percent), and miscellaneous (7 percent) (6).

Calcium chloride is usually sold either as solid flake or pellet averaging 75 percent $CaCl_2$, or as a concentrated liquid averaging about 40 percent $CaCl_2$ (6). The average value in 1980 for solid, natural calcium chloride was $92.09 per metric ton ($83.53 per short ton), whereas a recent selling price was listed as $145.50 per metric ton ($132.00/short ton) in 1983 (Chemical Marketing Reporter, 5/6/83).

As a consequence of the petition from the Salt Institute to review the sodium chloride subcategory, EPA decided to review the calcium chloride subcategory as well because the currently effective zero discharge BAT effluent limitations for the calcium chloride subcategory are based upon the same technology as the currently effective zero discharge BAT effluent limitations promulgated for the sodium chloride subcategory (replacement of barometric condensers with surface condensers) and because there are similarities in the processes.

Process Description

The calcium chloride is extracted from impure natural brines. In the manufacturing of calcium chloride from brine, the salts are solution mined and the resulting brines are first concentrated to remove sodium chloride by precipitation. Bromides and iodides are separated from the brines before sodium chloride recovery is performed. The brine is then purified by the addition of other materials to precipitate sodium, potassium, and magnesium salts. The purified calcium is flaked and calcined to a dry solid product. Extensive recycling of partially purified brine is used to recover most of the sodium chloride values.

A typical concentration of the brine is (2):

$CaCl_2$	19.3%	Bromides	0.25%
$MgCl_2$	3.1%	Other Minerals	0.5%
$NaCl$	4.9%	Water	70.8%
KCl	1.4%		

Water Use and Wastewater Characteristics

In 1974, one plant was visited and used as the basis of BPT limitations. At this plant, process wastewater resulted from process blowdown and from several partial evaporation steps. The effluent from this plant contained approximately 2,860 cubic meters/day (0.755 MGD) of washdown and washout water.

At this plant, the wastewater from all chemical manufacturing processes located at the site was treated in an activated sludge treatment plant to remove organic substances, and then passed to a settling basin to remove suspended matter. The pH was then adjusted and the water passed to a second pond to further settle suspended matter, and finally discharged. In 1974, the plant planned on making a change in the evaporators to reduce or eliminate calcium chloride discharges and eliminate ammonia. More recycling of spent brines was also planned.

During a follow-up study in 1976, considerable changes had been made in the usage of water at this plant. Average total wastewater discharge (including noncontact cooling water) was reduced from 31,600 cubic meters per day (8.35 MGD) in 1974 to 11,550 cubic meters per day (3.05 MGD) in 1976. Currently (1983) the discharge consists solely of noncontact cooling water. A surface condenser was installed to eliminate discharges from a barometric condenser. The condensate from the surface condenser is now recycled and is estimated at approximately 1458 cubic meters per day (385,000 gpd). Approximately 955 m^3/day (252,000 gpd) of concentrated brine is returned to the formation.

In late 1982 and early 1983, a survey of all seven plants in this subcategory was conducted to determine the discharge status of all seven plants. The results of this survey and data gathered previously are listed below:

Plants	Zero Discharge[3]	Indirect Discharge[4]
7	7	0

This survey was conducted by consulting the 1982 SRI Directory of Chemical Producers (7), by telephone contact with each of the plants, review of the 1974 Development Document and the Phase I rulemaking record and a previous contractor's report (8).

There are no known dischargers in this industry.

Recommendations

BAT, NSPS, PSNS Effluent Limitations. Based upon the survey conducted, there are no known dischargers in this subcategory. All seven facilities already are achieving the BAT limitations of no discharge of process wastewater pollutants. Therefore, the Agency is not proposing any changes in the currently effective BAT effluent limitation.

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[3] Includes three plants known to be zero discharge and three others located in inland, arid areas; these facilities reinject waste brine because of a scarcity of process water available.

[4] All plants confirmed that they were not indirect dischargers or were located in rural areas with no POTW.

Similarly, since new sources can be designed for this requirement and avoid any retrofit, and the costs of surface condensers are similar to barometric condensers, there is no reason to amend NSPS or PSNS.

PSES Effluent Limitations. Since there are no indirect dischargers in this subcategory, the Agency proposes to exclude the subcategory from any development of PSES.

BCT Effluent Limitations. Since there are no existing dischargers, there is no need for a BCT.

SODIUM SULFITE

General

The major inorganic chemical process for sodium sulfite manufacture consists essentially of reacting sulfur dioxide with soda ash. Another source is as a by-product from the production of phenol or its derivatives through the reaction of sodium benzene sulfonate with sodium hydroxide. The latter process is an organic chemical process and is not included in this subcategory.

There are three sodium sulfite plants which utilize the soda ash - sulfur dioxide reaction process. The annual production capacity of sodium sulfite by this process is estimated to be approximately 69,840 metric tons (77,000 short tons) with an estimated total average daily discharge of 416.4 cubic meters (110,000 gpd). There are two direct dischargers and a single indirect discharger, which discharges an average of 70 cubic meters per day (18,500 gpd). This stream consists of slightly contaminated washdown water only.

At the time of promulgation of the sodium sulfite regulations, there were seven plants in the subcategory with a total annual production capacity of 181,000 metric tons (200,000 short tons) per year and a total average daily discharge of 568 cubic meters (0.15 MGD). However, as stated above, there are now only three plants included in the sodium sulfite subcategory, with a substantial decrease in capacity.

After receiving the petition from the Salt Institute to review the sodium chloride subcategory, EPA decided to reconsider the BAT for the sodium sulfite subcategory (soda ash -sulfur dioxide process). BAT for this subcategory requires no discharge of "process wastewater pollutants" except for excess water discharged from wastewater impoundments designed to contain the 25-year - 24-hour storm. BPT, however, allows a continuous discharge.

Process Description

In the soda ash-sulfur dioxide reaction process, sulfur dioxide gas is passed into a solution of sodium carbonate until the product is acidic. At this point the solution consists primilarly of sodium bisulfite which is converted to sodium sulfite by the further addition of soda ash and heat until all the carbon dioxide is released.

The crude sulfite formed from this reaction is purified, filtered to remove insolubles from the purification steps, crystallized, dried and shipped.

Water Use and Wastewater Characteristics

The process water generated in this subcategory consists primarily of evaporator/crystallizer condensate, condensed dryer vapor, filter washwater, and process cleanout water. Wastewater volumes are generally low, and for the three plants in this subcategory are as follows:

Plant	Capacity*	Direct/Indirect	Flow	Treatment
A	27,210 kkg	Direct	16.4 m^3	pH adjust, oxidation, filtration
B	33,560 kkg	Direct	330.0 m^3	pH adjust, oxidation, settling
C	9,070 kkg	Indirect	70.0 m^3	None
	69,840 kkg/yr		416.4 m^3/day	

Treatment technologies in use by the direct dischargers are equal to or better than those used in the sodium bisulfite subcategory.

Typical flows used for development of the BPT limitations were as follows:

	m^3/kkg
Process condensate	0.17
Dryer ejector and filter wash	0.29 - 0.63

The limitations were based upon the wastewater stream from the dryer ejector and filter wash operations at the high end of the range (0.63 m^3/kkg).

Data available for the three remaining plants utilizing the soda ash - sulfur dioxide reaction process yield an average unit flow of 2.2 m^3 kkg** (581 gal/ton) for all wastewater discharged.

BPT for this subcategory is oxidation of the sulfite to sulfate (usually by aeration) and filtration of the wastewater to remove suspended solids. BPT effluent limitations in effect are:

Parameter	Limitations (30 day average)	(24-hr Maximum)
pH	6-9	
TSS	0.016 kg/kkg	0.032 kg/kkg
COD	1.7 kg/kkg	3.4 kg/kkg

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*Reference 7
**Range: 0.22 m^3/kkg to 3.6 m^3/kkg

The treatment technology used as a basis for the zero discharge BAT limitations, NSPS, and PSNS was evaporation of the treated process wastewater. This technology was believed to be economically achievable based on 1971 fuel costs and the sale of the residue (sodium sulfate) from the evaporation. Those plants located in areas of the country where evaporation exceeded precipitation could use solar evaporation to achieve no discharge of process wastewater pollutants. However, for plants that cannot use solar evaporation, the cost of fuel has quadrupled since 1971, whereas the selling price of sodium sulfate has increased only slightly.

Review of Available Data

Data specific to the sodium sulfite industry are contained in the 1974 Development Document (Reference 2), and we also have data from sodium sulfite plants submitted to EPA in 1976-77 in response to our request for data under Section 308 of the Act.

The data specific to sodium sulfite contain limited information about the amount of toxic pollutants in the wastewater. However, the sodium sulfite production process is very similar to the production process for sodium bisulfite (compare the 1974 Development Document, pp. 154-8, with the 1982 Development Document, page 711). The major differences are that sodium

TABLE 17-4. TOXIC POLLUTANT CONCENTRATIONS OBSERVED IN TREATMENT EFFLUENT DURING VERIFICATION SAMPLING

Pollutant	Concentration (mg/l) Plant #987	Plant #586
Arsenic	ND	ND
Copper	0.27	ND
Zinc	0.010	ND
Cadmium	ND	ND
Chromium	0.11	ND
Lead	0.15	ND
Mercury	ND	0.010
Nickel	ND	0.050
Antimony	ND	0.020
Thallium	ND	ND
Silver	ND	ND

ND - Not Detected

sulfite is collected from the reaction mixture at a higher pH and that purification of the sodium sulfite, at least at one plant, includes the addition of small amounts of copper.

Since the raw materials are the same for sodium sulfite and sodium bisulfite, and since the unit flows are nearly the same (2.2 m^3/kkg for sodium sulfite and 1.5 m^3/kkg for sodium bisulfite), we estimated the total toxic pollutant load for the sodium sulfite industry based on the observed total toxic pollutant loads found at sodium bisulfite plants, with allowance for a slightly higher flow for sodium sulfite and for the use of copper during purification of sodium sulfite (these factors increased estimated raw waste loads above those observed at sodium bisulfite plants). We also considered the fact that both direct discharge plants reported in their responses to our 1976 request for data that the plants have treatment systems identical to those used in the sodium bisulfite industry. Those treatment systems do control discharges of toxic metals and chemical oxygen demand (COD). In addition, sodium sulfite and sodium bisulfite wastewaters are commingled for treatment in common treatment plants at both of those facilities.

Table 17-4 summarizes the toxic pollutant concentration data observed in treated effluent during verification sampling from the two sodium bisulfite plants visited during Phase I. Both plants employ hydroxide precipitation, aeration, and settling. All toxic metal levels are below detection levels or are marginally treatable by the technologies examined elsewhere in this document for metal salts production. All concentrations listed in the table are below the proposed BPT and BAT limitations for the same parameters listed in Sections 11 through 16.

Comparison of Sodium Sulfite and Sodium Bisulfite Subcategories

The discussion above points out the similarity between the Sodium Sulfite and Sodium Bisulfite Subcategories. Our review of both subcategories has shown that the processes and raw materials for the two chemicals are the same. In the case of sodium sulfite the process is taken further to completion. Examination of the wastewater flows shows that the unit flows for the two processes were nearly identical (1.5 m^3/kkg vs. 2.2 m^3/kkg), and the wastewater treatment technology in use at the plants was identical. In addition, both of the direct discharge sodium sulfite plants also produce sodium bisulfite and the wastewaters are commingled in a common treatment system. Table 17-5 is a summary and comparison of the two subcategories pointing out the similarities between them.

TABLE 17-5. Comparison of Sodium Sulfite and Sodium Bisulfite Subcategories

	Sodium Sulfite	Sodium Bisulfite
Plants	3	7
Unit Flow	2.2 m^3/kkg	1.5 m^3/kkg
Process	Soda Ash - SO_2	Soda Ash - SO_2
Raw Materials	$NaCO_3$, SO_2	$NaCO_3$, SO_2
Treatment Tech. In Place	OH Pptn., Aeration, Filt. or Settling	OH Pptn., Aeration Settling
BAT	Zero Discharge (1)	Discharge subject to 40 CFR 415.542

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(1) Eliminated by the final rule.

TABLE 17-6. WATER EFFLUENT TREATMENT COSTS AND RESULTING WASTE-LOAD CHARACTERISTICS FOR MODEL PLANT

SUBCATEGORY: Sodium Sulfite

ANNUAL PRODUCTION: A-27,210; B-33,560; C-9,070 METRIC TONS

DAILY FLOW: A-16.4; B-330; C-70 CUBIC METERS

PLANT AGE: N/A YEARS PLANT LOCATION: DE, VA, CA

a. COST OF TREATMENT TO ATTAIN SPECIFIED LEVELS

COST CATEGORY	COSTS ($1,000) TO ATTAIN LEVEL 1 Plant A	 Plant B	 Plant C
Facilities			
Installed Equipment (Including Instrumentation)	$152.6	$1,012.8	$373.8
Engineering	30.5	202.6	74.8
Contractor Overhead and Profit	27.5	182.3	67.3
Contingency	21.1	139.8	51.6
Land	-	-	-
Total Invested Capital	$231.7	$1,537.5	$567.5
Annual Capital Recovery	37.7	250.2	92.3
Annual Operating and Maintenance (Excluding Residual Waste Disposal)	180.4	1,622.2	399.7
Residual Waste Disposal	32.9	674.5	144.5
Total Annual Cost	$251.0	$2,546.9	$636.5

b. RESULTING WASTE-LOAD CHARACTERISTICS

Parameter	Avg. Conc. BPT	Effluent Loading kg/kkg After Treatment To Level A	 B	 C
TSS	0.016 kg/kkg	0	0	0
COD	1.7 kg/kkg	0	0	0
TDS	70,000-90,000 mg/l	0	0	0

c. TREATMENT DESCRIPTION

PLANT A: Evaporation - Agitated Falling-Film Evaporator (to dryness)

PLANT B: Evaporation - Multiple Effect Evaporator plus Agitated Falling-Film Evaporator

PLANT C: Evaporation - Multiple Effect Evaporator plus Agitated Falling Film Evaporator

Treatment Cost Estimates

Based upon last quarter 1982 costs, treatment cost estimates were prepared for the three existing plants. The only technology considered was evaporation because the existing BAT was based upon this technology. Table 17-6 summarizes the cost data developed.

Based upon these estimates, installation of the existing BAT technology at all three plants would require the following investment:

Total Capital Costs	$1,916,200
Total Annual Costs	$2,817,100[5]

Based on these costs, our Economic Impact Analysis for this subcategory predicts at least two plant closures and severe impacts for the other plant assuming the one indirect discharger had to comply with the currently effective BAT. Considering that the existing data base indicates low levels of toxic pollutants in treated effluent, we conclude that the costs associated with the existing BAT are not reasonable and that no discharge is not economically achievable. Therefore, we are withdrawing the existing BAT and establishing a new BAT for toxic pollutants equal to BAT for sodium bisulfite. Further justification for this proposal is provided by the similarity in processes, raw materials, treatment systems and wastewater flow for the two subcategories. The limitations for TSS and COD would remain the same based upon the same BPT technology.

Basis for BCT Effluent Limitations

On October 29, 1982 EPA proposed a new and revised methodology for determination of BCT for conventional pollutants (47 FR 49176). The methodology has been described in detail in several preceding sections. (See for example, Section 16 -"Basis for BCT Effluent Limitations").

Only one candidate BCT technology has been tested in this subcategory namely, the use of evaporation to eliminate all wastewater and contained TSS, total dissolved solids, COD and metals. TSS is the only conventional pollutant in the wastewater. Filtration was not tested as a candidate technology

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[5] Annual costs include energy costs which are very high for the BAT technology (evaporation).

TABLE 17-7. BAT AND BCT EFFLUENT LIMITATIONS FOR SODIUM SULFITE

Conventional(4) Pollutants	Effluent Limitations (kg/kkg)	
	30-day avg.	24-hour max.
pH	(1)	(1)
TSS	0.016(2)	0.032(2)
Non-Conventional Pollutants		
COD	1.7(2)	3.4(2)
Toxic Pollutants		
Chromium (T)	0.00063(3)	0.0020(3)
Zinc (T)	0.0015(3)	0.0051(3)

(1) Within the range 6.0 to 9.0.

(2) Based upon BPT promulgated for Sodium Sulfite Subcategory (40 CFR Sec. 415.202).

(3) Based upon BAT promulgated for Sodium Bisulfite Subcategory (40 CFR Sec. 415.542).

(4) BCT only.

because the BPT limitations were based upon hydroxide precipitation, aeration, and filtration.

The amount of TSS removed by the candidate technology may be calculated from the BPT limitations and production capacity for the subcategory:

$$(0.016\ \text{kg/kkg})\ (69,840\ \text{kkg/yr}) = 1,117.4\ \text{kg/yr}\ (2,458.4\ \text{lbs.})$$

Therefore:

$$\frac{\$2,817,100/\text{yr}}{1,117.4\ \text{kg/yr}} = \$2,512.12/\text{kg TSS removed} \div 2.2\ \text{lb/kg}$$

$$= \$1,141.87/\text{lb TSS removed (1982)}$$

On October 29, 1982, EPA proposed a revised BCT methdology. While EPA is considering revising that proposed methdology, we have determined that in this subcategory no technology beyond BPT will pass the proposed BCT cost test or any other BCT test that the Agency is likely to adopt. Accordingly, EPA has determined that BCT equals BPT in this subcategory. Therefore, EPA is promulgating BCT equal to BPT.

Basis for BAT Effluent Limitations

Since BPT is already in effect for this subcategory, the Agency evaluated its effectiveness for removal of toxic metals as well as the effectiveness of similar BPT and BAT systems which form the basis of limitations for the sodium bisulfite subcategory. In addition, the costs were reevaluated for the technology used as the basis for the 1974 BAT effluent limitations. Using the data presented earlier and these cost estimates for evaporation, it was concluded that the BAT effluent limitation of zero discharge for this subcategory should be withdrawn.

In its place, the Agency is promulgating effluent limitations for toxic metal and non-conventional pollutants based upon the BPT technology. Additional parameters, chromium and zinc, are added, and these limitations are based upon the limitations already in effect for the sodium bisulfite subcategory.*

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*Although one facility adds small amounts of copper in the process, this parameter will be effectively controlled by the technology upon which the limitations for the other toxic metal parameters are based.

Table 17-7 summarizes the limitations promulgated for this subcategory.

Since the evaporation technology is not economically achievable and since the raw materials, processes employed, treatment systems, unit flows, and toxic pollutant concentrations are similar, we are basing the promulgated limits for toxic pollutants on the existing BAT for sodium bisulfite. We are not changing the limitations established for COD under BPT because the BAT limitations are based upon the BPT technology.

Basis for NSPS Effluent Limitations

Since the evaporation technology is not economically achievable, a no discharge limitation would be a barrier to entry. For NSPS, the Agency is promulgating limitations equal to BAT since there is no other technology known which would remove significant additional amounts of pollutants. For TSS and COD, the limitations are the same as BPT since the technology basis for BAT is the same as for BPT.

Basis for Pretreatment Standards

Pretreatment is necessary because it provides better removal of chromium, zinc, and COD than is achievable by a well operated POTW with secondary treatment installed, and thereby prevents pass-through that would occur in a POTW in the absence of pretreatment.

The Agency does not have raw waste load data for sodium sulfite manufacturing but does have such data for sodium bisulfite manufacturing. Because of the similarities in the processes and wastewater sources, the sodium bisulfite raw waste load data for COD, chromium, and zinc have been used as the raw waste loads expected from sodium sulfite manufacturing. These concentrations are compared to the treated effluent long-term average concentrations for the selected BAT technology for sodium sulfite to estimate the percent removals for COD, chromium, and zinc. The calculations are as follows:

COD: Raw Waste = 1960 ppm
BAT = 550 ppm

$$\text{Percent Removal} = [(1960-550)\div(1960)](100) = 71.9\%$$

Chromium: Raw Waste = 1.95 ppm
BAT = 0.22 ppm

Percent Removal = [(1.95-0.22)÷(1.95)](100)
= 88.7%

Zinc: Raw Waste = 1.81 ppm
BAT = 0.52 ppm

Percent Removal = [(1.81-0.52)÷(1.81)](100)
= 71.3%

The percent removals of chromium, zinc, and COD are greater than the removals for chromium (65%), zinc (65%), and COD (72%) achieved by 25% of the POTWs in the "50 Cities" study (see Fate of Priority Pollutants in Publicly Owned Treatment Works, Final Report, Volume I, EPA-440/1-82-303, September 1982). Therefore, chromium, zinc, and COD would pass through a POTW in the absence of pretreatment.

Existing Sources

There is one indirect discharger in this subcategory which discharges 70 cubic meters per day (18,500 gpd) to a POTW. Total toxic metal pollutant loading for this single facility are estimated to be 0.053 kg/day (0.12 lb/day). This estimate is based on the COD data provided by the Plant. That data shows that the average COD discharge is less than the long-term average COD used to develop the COD effluent limitations. Since the toxic metals are in the wastewater with the COD, the toxic metals are also estimated to be low in concentration and about equal to their long-term average concentrations. On the basis of flow and low toxic pollutant loading, we are excluding this subcategory from further PSES development under Paragraph 8(b)(ii) of the EPA-NRDC Settlement Agreement.

New Sources

The Agency is promulgating PSNS that are equal to NSPS because these standards provide for the removal of toxic metals which may pass through a well operated POTW with secondary treatment in the absence of pretreatment. The pollutants regulated under PSNS are chromium, zinc, and COD. Table 17-6 summarizes the PSNS limitations for chromium, zinc, and COD.

SECTION 17

REFERENCES

1. U.S. Bureau of Mines, "Directory of Companies Producing Salt in the United States - 1981," Mineral Industry Surveys, prepared in the Division of Industrial Materials.

2. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganic Products segment of the Inorganic Chemicals Manufacturing Point Source Category," EPA-440/1-74-007a, March 1974.

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4. Peters, M.S. and Timmerhaus, K.D., "Plant Design and Economics for Chemical Engineers," Third edition, McGrawHill Book Co., 1980.

5. Chemical Marketing Reporter, "Chemical Profile - Calcium Chloride," December 25, 1978.

6. U.S. Bureau of Mines, "Minerals Yearbook - 1980," Vol. I, Meals and Minerals.

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8. "Supplement for Pretreatment to the Development Document for the Inorganic Chemicals Manufacturing Point Source Category," EPA 440/1-77/087.

9. Terlecky, P.M. and Harty D.M., "Status of Group II Chemical Subcategories of the Inorganic Chemicals Manufacturing Industry of (Phase II)," Frontier Technical Associates, Inc. Report No. FTA-82-E-2/03 Revised January 14, 1983.

SECTION 18

PRETREATMENT STANDARDS FOR DEFERRED SUBCATEGORIES

INTRODUCTION

General

As part of Phase II, EPA considered pretreatment standards for 23 additional subcategories of the Inorganic Chemicals Point Source Category. For 18 of these subcategories, PSES had not been promulgated. Therefore, for these 18 subcategories, the purpose of this review was to determine which subcategories might require development of PSES. For the remaining five subcategories, the purpose of the review was to determine whether existing pretreatment standards were adequate.

Pretreatment Standards for New Sources (PSNS) requiring zero discharge are currently in effect for 10 of those 23 subcategories. Of the remaining 13 subcategories, one is covered under the Petroleum Refining Point Source Category (Hydrogen). Each of the 12 subcategories not covered by PSNS is currently subject to a zero discharge BPT requirement.

Subcategories Surveyed

The 23 subcategories surveyed are as follows:

1. Borax
2. Bromine
3. Calcium Carbide**
4. Calcium Chloride**
5. Chromic Acid
6. Fluorine
7. Hydrogen***
8. Iodine
9. Calcium Oxide**
10. Calcium Hydroxide
11. Potassium Chloride
12. Potassium (metal)**
13. Potassium Sulfate**
14. Sodium Bicarbonate**
15. Sodium Chloride**
16. Sodium Sulfite**
17. Stannic Oxide
18. Zinc Sulfate
19. Aluminum Sulfate*,**
20. Ferric Chloride*
21. Lead Monoxide*
22. Potassium Dichromate*,**
23. Sodium Fluoride*

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*Subcategories with existing PSES.
**Subcategories with existing PSNS.
***Subcategory covered by Petroleum Refining Category.

Methods Employed

An accurate and up-to-date list of all companies and plants which manufacture the products in the 23 subcategories was developed. Sources utilized in compiling that list included: the Stanford Research Institute's "Directory of Chemical Producers - 1982" (1) the OPD Chemical Buyers Directory (2), the Salt Institute's membership list, the U.S. Bureau of Mines (3), the Lime Association, the Thomas Register, in-house files at EPA and the contractor, and a previous EPA survey. All plants identified from the above sources were contacted to determine which plants and facilities in each subcategory were indirect dischargers. Some of the plants initially identified were subsequently determined to be distributors or repackagers and were not producing the chemical.

The several sources listed above identified 304 plants in 22 subcategories (all except the Hydrogen subcategory). Information on 302 of those plants was provided through telephone or written contacts with the plants, by Regional and State NPDES permit authorities, and from local POTW authorities. The two plants which could not be contacted are located in remote, rural areas where there are no POTW's. For the hydrogen subcategory (refinery by-product), there are 137 plants listed in addition to those above. However, any discharges to POTW's are controlled under existing PSES and PSNS for the Petroleum Refining Subcategory (40 CFR Part 419).

Basis for PSES Exclusions

Paragraph 8(a)(i) of the Settlement Agreement authorizes the Administrator to exclude from regulation industrial categories or subcategories for which equal or more stringent limitations are already provided by existing effluent limitations and standards (in this case, the Hydrogen Subcategory). Paragraph 8(b) of the Settlement Agreement authorizes the Administrator to exclude from regulation under the pretreatment standard a subcategory if (i) 95 percent or more of all point sources in the subcategory introduce into POTWs only pollutants which are susceptible to treatment by the POTW and which do not interfere with, do not pass through, or are not otherwise incompatible with such treatment works; or (ii) the toxicity and amount of the incompatible pollutants introduced by such point sources into POTWs is so insignificant as not to justify developing a pretreatment regulation.

SURVEY RESULTS BY SUBCATEGORY

This section summarizes the results obtained for the 23 subcategories surveyed. Subcategories 1 through 18 have no current PSES proposed or promulgated. For the remaining five subcategories (19-23), PSES have been promulgated.

Subcategories 1-18

1. Borax

There are four known producers of borax (sodium tetraborate) by the mining process or Trona process. There are no indirect dischargers in this subcategory because all facilities use evaporation ponds for process wastewater.

2. Bromine

There are eight known producers of bromine by the brine mining process and by the Trona process. There are no indirect dischargers.

3. Calcium Carbide

There are three known producers of calcium carbide from uncovered furnaces. There are no indirect dischargers in this subcategory. Calcium carbide from covered furnaces is regulated under the Ferroalloys Category at 40 CFR 424.40 and 424.50.

4. Calcium Chloride

There are seven known producers of calcium chloride by the brine extraction process. There are no direct or indirect dischargers in this subcategory.

5. Chromic Acid

There are two known producers of chromic acid in facilities which also manufacture sodium dichromate (see 40 CFR 415.350). There are no indirect dischargers in this subcategory.

6. Fluorine

There are two known producers of fluorine by the liquid hydrofluoric acid electrolysis process. There are no indirect dischargers in this subcategory.

7. Hydrogen

There are approximately 137 plants producing hydrogen as a by-product of the petroleum refining process. Wastewater from this subcategory is subject to effluent limitations for the Petroleum Refining Point Source Category (40 CFR 419).

8. Iodine

There are three known producers of iodine but only one plant discharges to a POTW. That one plant discharges approximately 200 gpd to a POTW.

9. Calcium Oxide (Lime)

There are 50 known facilities producing calcium oxide (lime). There are no indirect dischargers. One plant could not be contacted but is located in a remote, rural area far from a POTW.

10. Calcium Hydroxide (Hydrated Lime)

There are 37 known producers of hydrated lime. One of these discharges to a POTW, and two discharge directly. A total of 33 facilities achieve zero discharge because they are dry operations, by recycle, and by impoundment and evaporation. The discharge status of one facility is unknown, but it is located in a remote, rural area far from a POTW. The single indirect discharger discharges only 200 gallons/day (10 gpm for 20 min.) to a POTW.

11. Potassium Chloride

There are eight known producers of potassium chloride by the Trona process and by the mining process (40 CFR 415.500) at present. There are no indirect dischargers in this subcategory.

12. Potassium (Metal)

There is one known producer in this subcategory which does not discharge process wastewater from potassium metal manufacturing to a POTW.

13. Potassium Sulfate

There are six known producers of potassium sulfate none of which discharge to POTWs.

14. Sodium Bicarbonate

There are four known plants producing sodium bicarbonate. Three plants do not discharge process wastewater while one plant commingles wastewater from sodium bicarbonate production with other process wastewater, treats it and then discharges to a POTW.

With regard to the single indirect discharger, the following monitoring information was obtained from the POTW concerning toxic metal concentrations in the discharge to the POTW from the plant (for a period 13 months)(from Reference 6):

Parameter
Average Concentration (mg/l)

Cd	Cr	Cu	Pb	Hg	Ni	Ni
<0.017	0.018	0.051	<0.029	<0.0011	0.026	0.076

Toxic metals in the discharge are present at concentrations which are low and near detection levels.

15. Sodium Chloride

Sodium chloride is produced by both the solution brine-mining and solar evaporation processes. The results of the survey of plants employing both processes are included here.

a. Solution Brine Mining. There are 18 known producers of sodium chloride by the solution brine mining process. None of these plants discharge to POTWs.

b. Solar Evaporation Process. There are 39 known producers of sodium chloride by the solar evaporation process. There are no indirect dischargers.

Both processes (a and b) are employed at some facilities.

16. Sodium Sulfite

There are three known producers of sodium sulfite by reacting sulfur dioxide with sodium carbonate (soda ash). Two of these discharge wastewater directly while one facility discharges washdown water only to a POTW (70 cubic meters per day (18,500 gpd)). On the basis of the information and analysis presented in Section 17 of this report, the Agency is excluding this subcategory from PSES.

17. Stannic Oxide

There is one known producer of stannic oxide. This facility uses a dry thermal process which involves the reaction of tin metal with air or oxygen. No wastewater is produced and there is no discharge.

18. Zinc Sulfate

There are 12 known producers of zinc sulfate. There are two indirect dischargers. One of these discharges an average of 4000 gpd to the POTW. Flows are less than 1 percent of plant flow. The zinc sulfate process discharge at the second plant amounts to less than 350 gpd, which is less than 1 percent of total plant discharge to the POTW.

Subcategories 19-23

This group of five categories represents chemicals for which PSES are already in effect. The purpose of this review was to determine if the current regulatons are adequate for control of toxic pollutants.

19. Aluminum Sulfate

There are 70 known producers of aluminum sulfate at present. Of these, only two discharge indirectly. One of these two plants discharges less than 1000 gallons per year to the POTW, while the discharge to a POTW from the second is in compliance with the currently effective PSES.

PSES In Effect. Current PSES in this subcategory are as follows:

Parameter	PSES (30-day avg./24-hr. max.)
Zinc (Total)	2.5/5.0 mg/l

Since these concentrations are similar to those promulgated for other subcategories in Phase I, the existing PSES are believed to be adequate.

20. Ferric Chloride

There are eight known producers of ferric chloride from pickle liquor. Only one plant in this subcategory currently discharges indirectly while four achieve zero discharge.

PSES in Effect. Current PSES in this subcategory are as follows:

Parameter	PSES (30-day avg./24-hr. max.)
Cr (Total)	1.0/3.0 mg/l
Cr (VI)	0.09/0.25 mg/l

Cu (Total)	0.5/1.0 mg/l
Ni (Total)	1.0/2.0 mg/l
Zn (Total)	2.5/5.0 mg/l

These concentrations are similar to those promulgated for other subcategories in Phase I. Therefore, the existing PSES are believed to be adequate.

21. Lead Monoxide

There are nine known producers of lead monoxide in the U.S. There are no direct or indirect dischargers of process wastewater in this subcategory. Lead monoxide is produced by a dry process and produces no wastewater.

PSES In Effect. Current PSES in this subcategory are as follows:

Parameter	PSES (30-day avg./24-hr. max.)
Pb (Total)	1.0/2.0 mg/l

These concentrations are similar to those promulgated for other subcategories in Phase I. Therefore, the existing PSES are believed to be adequate.

22. Potassium Dichromate

There is one plant in this subcategory. The plant achieves no discharge by total recycle of process wastewater.

PSES in Effect. Current PSES in this subcategory are as follows:

Parameter	PSES (30-day avg./24-hr. max.)
Cr (VI)	0.090/0.25 mg/l
Cr (Total)	1.0/3.0 mg/l

These concentrations are similar to those promulgated for other subcategories in Phase I. Therefore, the existng PSES are believed to be adequate.

23. Sodium Fluoride

There are four known producers of which two discharge indirectly.

PSES in Effect. Current PSES in this subcategory are as follows:

Parameter	PSES (30-day avg./24-hr. max.)
Fluoride	25/50 mg/l

One plant is known to produce less than 1000 pounds per year of sodium fluoride, which would generate an insignificant flow. Control of fluoride, as required by the PSES, involves lime precipitation and clarification. This technology not only removes fluoride from the wastewater but also effects the removal of any toxic metal pollutants that may be present in the untreated wastewater. Therefore, the existing PSES are believed to be adequate.

EXCLUSIONS

The Agency is excluding the twelve subcategories listed below from national PSES regulation development under Paragraph 8 b(ii) of the Settlement Agreement because there are no indirect dischargers in the subcategory:

No Indirect Dischargers

Borax
Bromine
Calcium Carbide
Calcium Chloride
Chromic Acid
Fluorine
Calcium Oxide (Lime)
Potassium Chloride
Potassium Metal
Potassium Sulfate
Sodium Chloride
Stannic Oxide

The Agency is excluding the following subcategories from PSES development under Paragraph 8 (b)(ii) because the discharge to POTW from the one indirect discharger in each subcategory is so insignificant due to low flow or low quantities of toxic pollutants:

One Indirect Discharger

Iodine
Hydrated Lime
Sodium Bicarbonate
Sodium Sulfite (See also Section 17)

TABLE 18-1. SUMMARY OF THE DISCHARGE STATUS OF ALL PSES SUBCATEGORIES

		Plants	Other**	Discharge Method Indirect	Discharge Method Unknown
1.	Borax	4	4	0	0
2.	Bromine	8	8	0	0
3.	Calcium Carbide	3	3	0	0
4.	Calcium Chloride	7	7	0	0
5.	Chromic Acid	2	2	0	0
6.	Fluorine	2	2	0	0
7.	Hydrogen	*(137)	*	*	*
8.	Iodine	3	2	1	0
9.	Lime	50	49	0	1(1)
10.	Hydrated Lime	37	35	1	1(1)
11.	Potassium Chloride	8	8	0	0
12.	Potassium (Metal)	1	1	0	0
13.	Potassium Sulfate	6	6	0	0
14.	Sodium Bicarbonate	4	3	1	0
15.	Sodium Chloride (brine)	22	22	0	0
	Sodium Chloride (evap.)	39	39	0	0
16.	Sodium Sulfite	3	2	1	0
17.	Stannic Oxide	1	1	0	0
18.	Zinc Sulfate	12	10	2(2)	0
19.	Aluminum Sulfate(3)	70	68	2	0
20.	Ferric Chloride(3)	8	7	1	0
21.	Lead Monoxide(3)	9	9	0	0
22.	Potassium Dichromate(3)	1	1	0	0
23.	Sodium Fluoride(3)	4	2	2	0

*Covered by petroleum refining guidelines
**Zero, direct, but not POTW

(1) One plant unable to be contacted, thought to be zero or direct.

(2) Flow at both plants is low, and less than 1% of plant flow to POTW.

(3) PSES currently in effect.

The zinc sulfate subcategory has two indirect dischargers. However, the total flow of both plants is very low (15.9 cubic meters per day (4200 gallons per day)) and in each case is less than 1 percent of the plant total daily flow to the POTW. The Agency is excluding this subcategory from categorical PSES for zinc sulfate under Paragraph 8 b(ii).

The Hydrogen (By-product from Petroleum Refining) subcategory is included under the promulgated PSES for the Petroleum Refining Point Source Category.

Subcategories with PSES In Effect

Information was developed during the survey to show that the PSES in effect are adequate, therefore, no change is promulgated for the PSES following five subcategories:

Aluminium Sulfate
Ferric Chloride
Lead Monoxide
Potassium Dichromate
Sodium Fluoride

PSNS

The 12 subcategories for which no PSNS are currently in effect are:

Borax
Bromine
Chromic Acid
Fluorine
Iodine
Calcium Hydroxide
Potassium Chloride
Stannic Oxide
Zinc Sulfate
Ferric Chloride
Lead Monoxide
Sodium Fluoride

Each of the above subcategories is currently subject to a zero discharge requirement under BPT. Therefore, a PSNS equal to BPT would not be a barrier to entry since existing plants are required to achieve zero discharge of process wastewater pollutants and meet that requirement.

The Agency is promulgating PSNS for each subcategory based upon the currently effective BPT, which for each subcategory requires zero discharge of process wastewater pollutants.

There are also no New Source Performance Standards (NSPS) for these 12 subcategories. However, none are needed since, in the absence of an NSPS, a new plant is subject to the currently effective BPT effluent limitations of zero discharge of process wastewater pollutants.

SECTION 18

REFERENCES

1. SRI International, 1982 Directory of Chemical Producers United States of America, SRI Menlo Park, California.

2. Chemical Marketing Reporter, 1983 OPD Chemical Buyers Directory, 70th ed., Schnell Publishing Co., New York (1982).

3. U.S. Bureau of Mines, "Directory of Companies Producing Salt in the United States - 1981," Division of Industrial Minerals, Mineral Industry Surveys, 10 p.

4. Calspan Corporation, Addendum B-1 (Background Data) to "Supplement for Pretreatment to Development Documents for the Inorganic Chemicals Manufacturing Point Source Category," Calspan Report No. ND-5782-M-85, 17 March 1977 (Survey conducted in 1976).

5. Terlecky, P.M. and Harty, D.M., "Status of Group II Chemical Subcategories of the Inorganic Chemicals Manufacturing Industry - Phase II," Frontier Technical Associates, Inc. Report No. FTA-82-E2/03, January 14, 1983.

6. Terlecky, P.M., Personal Communication, Letter to Dr. T. Fielding, (USEPA, May 17, 1983 (A summary of data supplied by the New York DEC, Region 2).

SECTION 19

EXCLUDED SUBCATEGORIES

INTRODUCTION

The Inorganic Chemicals Manufacturing Point Source Category has been divided into 184 subcategories for regulatory purposes. On June 29, 1982 the Agency promulgated effluent limitations guidelines and standards for or excluded from regulation 60 of those subcategories (the Phase I guidelines). The Agency is now promulgating effluent limitations guidelines and standards for 17 additional subcategories (the Phase II guidelines). The Agency is excluding 106 of the remaining 107 subcategories from national regulation development. One subcategory is deferred for regulation under another, more appropriate guideline.

The determinations in this section complete the examination required by the Settlement Agreement of all remaining subcategories covering the chemical products listed under SIC Codes 2812, 2813, 2816, and 2819. The methods used, sources examined, a summary of the determinations, and the rationale for the proposed exclusions are provided in this section.

Subcategories Surveyed

The 107 subcategories surveyed are listed in Table 19-1.

Methods Employed

An accurate and up-to-date list of all companies and plants which manufactured the products in the subcategories was compiled. Sources utilized include: The Stanford Research Institute's "Directory of Chemical Producers - 1982", (2) The OPD Chemical Buyers Directory (3), the Thomas Register, in-house files at EPA and the contractor and previous surveys for EPA. The purpose of this survey was to identify which plants and facilities were producing the individual chemicals, and to determine the discharge status of the plants in each subcategory. Some of the plants identified from the above sources were subsequently determined to be distributors or repackagers, and were not producing the chemical.

Information was obtained through telephone contacts with knowledgeable personnel at 269 plants. Additional information was gathered from 69 of those 269 plants through industry responses to EPA's requests for information under §308 of the Act. Engineering visits were made to 16 of the plants, and 14 of

Table 19-1. Inorganic Chemical Subcategories Surveyed

1. Aluminum Chloride
2. Aluminum Compounds
3. Aluminum Hydroxide (Hydrated Alumina)
4. Aluminum Oxide (Alumina)
5. Alums (also 6, 55, 77)
6. Ammonia Alum (also 5)
7. Ammonia Compounds
8. Ammonia Molybdate
9. Ammonia Perchlorate
10. Ammonia Thiosulfate
11. Barium Compounds
12. Barium Sulfate
13. Barytes Pigments
14. Beryllium Oxide
15. Bleaching Powder (Calcium Hypochlorite, No. 20)
16. Boron Compounds (not produced at mines)
17. Borosilicate
18. Brine Chemicals
19. Calcium Compounds (Inorganic)
20. Calcium Hypochlorite (Bleaching Powder, No. 15)
21. Cerium Salts
22. Chlorosulfonic Acid
23. Chrome Oxide (Chrome Pigments)
24. Chromium Sulfate
25. Deuterium Oxide (Heavy Water)
26. Hydrated Alumina Silicate Powder
27. Hydrogen Sulfide
28. Hydrophosphites
29. Indium Chloride
30. Industrial Gases
31. Inorganic Acids (except nitric and phosphoric acid)
32. Iodides
33. Iron Colors
34. Iron Oxide (Black) (Iron Oxide Pigments)
35. Iron Oxide (Magnetic) (Iron Oxide Pigments)
36. Iron Oxide (Yellow) (Iron Oxide Pigments)
37. Lead Arsenate
38. Lead Dioxide, Brown
39. Lead Dioxide, Red
40. Lead Silicate
41. Lithium Compounds
42. Magnesium Compounds, Inorganic
43. Manganese Dioxide (Powdered Synthetic)
44. Mercury Chloride
45. Mercury Oxide
46. Nickel Ammonium Sulfate
47. Nitrous Oxide
48. Ochers (Iron Oxide Pigments, No. 34-36)
49. Oleum (Sulfuric Acid)
50. Oxidation Catalyst made from Porcelain

Table 19-1. (continued)

51. Pechloric Acid
52. Peroxides (Inorganic)
53. Potash Alum (Potassium Aluminum Sulfate, also 5)
54. Potash Magnesia
55. Potassium Aluminum Sulfate (also 5, 53)
56. Potassium Bromide
57. Potassium Carbonate
58. Potassium Chlorate
59. Potassium Compounds, Inorganic
60. Potassium Cyanide
61. Potassium Hypochlorate
62. Potassium Nitrate and Sulfate
63. Rare Earth Metal Salts (Salts of Rare Earth Metals, No. 65)
64. Reagent Grade Chemicals
65. Salts of Rare Earth Metals (Rare Earth Metal Salts, No. 63)
66. Satin White Pigment
67. Siennas (Iron Oxide Pigments, No. 34-36)
68. Silica, Amorphous
69. Silica Gel
70. Silver Bromide
71. Silver Carbonate
72. Silver Chloride
73. Silver Cyanide
74. Silver Iodide
75. Silver Nitrate
76. Silver Oxide
77. Soda Alum (also 5)
78. Sodium Antimonate
79. Sodium Compounds, Inorganic
80. Sodium Cyanide
81. Sodium Hydrosulfite (Zinc Process)
82. Sodium Silicofluoride
83. Stannic and Stannous Chloride
84. Strontium Carbonate
85. Stronium Nitrate
86. Sulfide and Sulfites
87. Sulfocyanides (Thiocyanates also 91)
88. Sulfur
89. Sulfur Chloride
90. Sulfur Hexafluoride
91. Thiocyanates (also 87)
92. Tin Compounds
93. Ultramarine Pigments
94. Umbers (Iron Oxide Pigments, No. 34-36)
95. White Lead Pigment
96. Whiting (Calcium Carbonate)
97. Zinc Sulfide

Table 19-1. (continued)

Radioactive Materials:

98. Cobalt 60
99. Fissionable Materials
100. Isotopes, Radioactive (also 98)
101. Luminous Compounds (Radium) (also 105, 106)
102. Nuclear Cores, Inorganic (also 103)
103. Nuclear Fuel Reactor Cores, Inorganic (also 102)
104. Nuclear Fuel Scrap Reprocessing
105. Radium Chloride (also 101, 106)
106. Radium Luminous Compounds (also 101, 105)
107. Uranium Slugs, Radioactive

the 16 were sampled. Supplemental information was provided by NPDES permit authorities and by POTW authorities. The exclusions and other actions described in this section are based on the data acquired by the Agency through this survey.

EXCLUDED SUBCATEGORIES

Miscellaneous Inorganic Chemicals

1. Aluminum Chloride (Anhydrous). There are currently five plants in this subcategory. Two plants achieve zero discharge while two plants are direct dischargers and there is one indirect discharger. The two direct discharging plants discharge a total of less than 37.9 cubic meters per day (<10,000 gpd) of wastewater. Because of this low volume, the Agency does not expect significant amounts of toxic or nonconventional pollutants to be discharged and therefore is excluding the subcategory under the provisions of Paragraph 8 (a)(iv) because the amount and toxicity of each pollutant does not justify developing national regulations. PSES are currently in effect for this subcategory.

2. Aluminum Compounds. Specific aluminum compounds not addressed elsewhere are:

   a. Aluminum Nitrate - Three plants, low production (<4.5 kkg/yr (<10,000 lb/yr each)).

   b. Aluminum Silicate - There is one plant which has no discharge.

The Agency is excluding the above chemicals under Paragraphs 8(a)(iv) and 8(b) of the Settlement Agreement because (1) the low production results in low flow and thus loading; and (2) there is no discharge of process wastewater from the plant making the chemical.

3. Aluminum Hydroxide (Hydrated Alumina). The promulgated BPT and BAT limitations, NSPS and PSNS for hydrated alumina are contained in 40 CFR 421.10 (Subpart A - Bauxite Refining Subcategory of the Nonferrous Metals Manufacturing Point Source Category). Under the provisions of Paragraph 8 (a)(i), this subcategory is excluded from any further regulation development under the inorganic chemicals point source category because the wastewater from the plants in the subcategory is controlled by other effluent limitations guidelines and standards.

4. Aluminum Oxide (Alumina). BPT, BAT, NSPS, and PSNS limitations and standards have been promulgated (40 CFR 421.10 Subpart A - Bauxite Refining Subcategory of the Nonferrous Metals Manufacturing Point Source Category). Under the provisions of Paragraph 8 (a)(i), this subcategory is excluded from any further regulation development as part of the inorganic chemicals manufacturing point source category because the wastewater from the plants in the subcategory is controlled by other effluent limitations guidelines and standards. The current effluent limitations would continue to apply.

5. "Alums". This subcategory represents the consolidation of four subcategories as originally listed in Table 19-1: ammonia alum (No. 6), potash alum (No. 53), potassium aluminum sulfate (No. 55), and soda alum (No. 77). The subcategories were consolidated because production methods and probable pollutants are expected to be the same. There is only one producer of alums and that one plant does not discharge process wastewater.

   Therefore the Agency is excluding this subcategory under Paragraphs 8 (a)(iv) and 8(b)(ii) because there are no known dischargers.

6. Ammonia Alum. (See subcategory No. 5 above)

7. Ammonia Compounds. Specific ammonium compounds not addressed elsewhere are:

   a. Ammonium Bisulfite - There are three plants in this subcategory. Two plants achieve zero discharge. The remaining plant discharges about 10,000 gallons per year to a POTW. The Agency is excluding this chemical from national BAT regulation under Paragraph 8(a)(iv) of the Settlement Agreement. In addition, the single indirect discharger is excluded from categorical PSES under Paragraph 8(b)(ii) because the low flow is too insignificant to justify a national regulation.

   b. Ammonium Dichromate - There is only one plant in this subcategory. This plant, a direct discharger, also produces sodium dichromate and combines the wastewater for treatment and discharge. This chemical is excluded from national BAT and PSES regulation development under Paragraphs 8(a) (iv) and 8(b)(ii) of the Settlement Agreement based upon the fact that there is only one plant and there are no indirect dischargers.

c. Ammonium Fluoride - There is only one plant producing this chemical in quantity. This plant does not discharge process wastewater. Two other plants produce a very pure product (reagent grade) in very low quantities (<4.5 kkg/yr). Both of these plants achieve zero discharge. This chemical is excluded because there are no dischargers (Paragraphs 8(a)(iv) and 8(b)(ii)).

d. Ammonium Fluoborate - There is only one plant producing this chemical and that plant does not discharge process wastewater. This chemical is excluded under Paragraphs 8(a)(iv) and 8(b)(i) of the Settlement Agreement because there are no dischargers.

e. Ammonium Sulfide - There are two plants producing this chemical, but the product is produced in solution form only and no effluent is produced because all water used is incorporated into the product. This chemical is excluded under Paragraphs 8(a)(iv) and 8(b)(ii) of the Settlement Agreement because there is no discharge of process wastewater.

f. Ammonium Tungstate - There are two plants producing this chemical each employing a different production process. One of the facilities disposes of wastewater in an evaporation pond and achieves zero discharge. Therefore, there is only one discharging facility which is a direct discharger.

This chemical product is excluded based upon Paragraphs 8(a)(iv) and 8(b)(ii) of the Settlement Agreement because there is only one discharger.

8. Ammonium Molybdate. There are two plants producing this chemical. One plant has no discharge, while the second plants produces a reagent grade product in small amounts (<4.5 kkg/yr (<5 tons/yr)). This chemical is produced only intermittently. All plant wastewater is commingled with all other product wastewaters and treated in a treatment system equivalent to BAT technology prior to discharge. The Agency is excluding this subcategory Paragraphs 8(a)(iv) and 8(b)(ii) of the Settlement Agreement because there is only one discharger.

9. Ammonia Perchlorate. There are two plants producing this chemical and neither discharges to surface waters. Therefore, the Agency is excluding this subcategory under

Paragraphs 8(a)(iv) and 8(b)(ii) because there are no dischargers.

10. Ammonia Thiosulfate. The total toxic metal discharge from all 10 plants in the subcategory based upon screening and verification sampling is less than 0.27 kg/day (0.6 lb/day). Relevant data are presented in Table 19-2a. Five of the ten plants achieve zero discharge. No toxic organic pollutants were detected at treatable levels at these plants. Therefore, the Agency is excluding this subcategory under Paragraph 8(a)(iii), 8(a)(iv) and 8(b)(ii) of the Settlement Agreement.

11. Barium Compounds. Inorganic barium compounds are produced at a limited number of sites. Barium compounds not addressed elsewhere are:

   a,b. Barium Chloride, Barium Peroxide - All production of these chemicals occurs at three plants which also make barium carbonate. All three plants use the same wastewater treatment system for all barium chemicals produced. The combined wastewater was sampled in Phase I and no toxic pollutants were found at treatable levels during screening and verification sampling at one plant.

   c. Barium Sulfide - This chemical is produced exclusively as an intermediate in the overall process for barium carbonate. Barium carbonate was excluded under Phase I because no toxic pollutants were found at treatable levels during screening and verification sampling at one plant.

   d. Barium Hydroxide - This chemical is produced at four plants. The large producer achieves no discharge by an evaporation pond while the other three plants produce reagent grade chemicals with very low production. One of these plants is known to achieve zero discharge. The total discharge from the other two plants (one direct, one indirect discharger) is estimated to be about 10,000 gallons per year.

   e. Barium Nitrate - There are five producers of this chemical. The only bulk producer achieves no discharge by use of an evaporation pond. The other four plants produce reagent grade chemicals with very low production. One of these plants is known to achieve zero discharge. The other three plants (two direct and one indirect) are estimated to discharge a total of less than 10,000 gallons per year.

f. Barium Perchlorate - There are two plants producing this chemical. One achieves no discharge by recycle while the second discharges to a POTW. Production at the second plant is less than 2.3 kkg/yr (5000 lb/yr). Because of the very low production, discharges of toxic pollutants would be insignificant.

The Agency is excluding all of the above chemical products under Paragraphs 8(a)(iv) and 8(b)(ii) of the Settlement Agreement (low loading because of low flow).

12,13. Barium Sulfate, Barytes Pigments. In each subcategory there is only one plant which produces the chemical in bulk, and two other plants that have very low production rates. None of the small producers discharges process wastewater. The Agency is excluding each subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) because there is only one discharger in each subcategory. The Agency considered combining the subcategories because the products are very similar but the production processes, raw materials, and expected pollutants are significantly different for each plant. Hence combining the subcategories was not technically feasible.

14. Beryllium Oxide. This compound is produced at one site as part of the production process for beryllium metal or beryllium-copper alloys. This subcategory is deferred for coverage under limitations and standards to be established for the Non-Ferrous Metals Category (40 CFR Part 421). A new study of this category by EPA is currently underway.

15. Bleaching Powder (also Calcium Hypochlorite, No. 20). See Subcategory No. 20. Note that sodium perborate is sometimes also referred to as bleaching powder. Sodium perborate is addressed under Sodium Compounds (Subcategory No. 79).

16. Boron Compounds (Not produced at Mines). Inorganic boron compounds not addressed elsewhere are:

a. Boron Trifluoride - Two plants produce this chemical on a specialty basis with very low production. Generally, this chemical would be produced two or three times per year in small batches. Little flow is expected beside process cleanup, leaks, and spills. Any wastewater produced is treated in the plant treatment system for other chemical production. Both plants are direct dischargers with a total discharge estimated to be 5,000 gallons per year.

b. Boron Trichloride - One plant produces this chemical and utilizes an evaporation pond to achieve no discharge of process wastewater.

c. Boron Hydrides - There is only one plant producing this chemical on a specialty basis with very low production.

d. Boron Nitride - There are three plants producing this chemical at present. All three discharge to a POTW but flows are low (two plants discharge less than 3.8 cubic meters per day each (<1000 gpd). The third plant flow is unknown but is expected to be similar (and low) to the other producers because process technologies are known to be similar. Hence, the total flow is estimated to be about 3,000 gallons per day.

e. Sodium Borohydride - The production of this chemical is a non-aqueous process with no discharge of process wastewater. There are two plants currently manufacturing this chemical but there are no dischargers.

f. Lithium Metaborate - This chemical is produced at two plants on a specialty basis with low production. No priority pollutants are known to be involved in its production. One plant achieves zero discharge of process wastewater. The other plant is estimated to discharge less than 2,000 gallons per year directly to surface waters.

All of the above chemicals are produced in small quantities at few plants with little or no wastewater flow. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) (low production, low flow and loading).

17. Borosilicate. This chemical is no longer produced in this country. Therefore the Agency is excluding this subcategory from further regulatory consideration under Paragraphs 8(a)(iv) and 8(b)(ii).

18. Brine Chemicals. Brine refers to strong salt solutions. This subcategory has been interpreted to mean chemicals produced from brine. Most of these chemicals have been considered separately (e.g., calcium chloride, sodium

chloride). Four salts which have not been considered separately are sodium, calcium, potassium and ammonium bromide.

There are five plants producing these four products. However, only two plants (direct dischargers) have a discharge of process wastewater. Screening and verification sampling at one of those two plants show that no toxic or nonconventional pollutants were found at treatable levels. Relevant data are presented in Table 19-2b. Most plants return spent brines to their source without addition of toxic materials, because the process is primarily an extractive one.

The Agency is excluding this subcategory under Paragraphs 8(a)(iii), 8(a)(iv) and 8(b)ii) because no toxic or nonconventional pollutants were detected at treatable levels.

19. Calcium Compounds (Inorganic). Inorganic calcium compounds not addressed elsewhere are:

a. Calcium Iodate - There are four plants producing this chemical but only one is a bulk producer. This plant does not discharge process wastewater from this product. The other three produce a reagent grade product in very low quantities and one of the three small plants does not discharge. The two dischargers (one direct and one indirect) are estimated to discharge a total of less than 5,000 gallons per year.

b. Calcium Nitrate - This chemical is produced only as a reagent grade material at three locations, therefore production quantities are low with little wastewater generated. Only one of those three plants discharges process wastewater. Since the raw materials are lime or calcium carbonate and nitric acid, chemical grade raw materials would be used producing little toxic pollutants.

c. Calcium Stannate - There are three plants producing this chemical with only two dischargers, one direct and one indirect. The two plants produce limited quantities of the chemical as a specialty product and the total discharge from both plants is estimated to be less than 10,000 gallons per year.

d. Calcium Tungstate - There are two plants producing this chemical but only one discharger (indirect). That plant produces the chemical on a specialty basis in small quantities. No priority pollutants are involved in its production. The total discharge is estimated to be less than 5,000 gallons per year.

All of the above chemical products are produced primarily by plants which supply reagent or specialty chemicals and hence produce in small quantities only. There are only two plants (each producing a separate chemical) which produce any of the chemicals in bulk quantities. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) (few plants, low production, low flow and loading).

20. Calcium Hypochlorite (Bleaching Powder). There are four producers, one of which is a paper mill, and the other three are chlor-alkali plants.

Screening and verification sampling at the paper mill (an indirect discharger) showed no toxic pollutants were discharged at treatable levels. Relevant data are presented in Table 19-2c (Plant A). Total Residual Chlorine is discharged at treatable levels, but the Agency has not regulated discharges of total residual chlorine to POTWs because POTW influent is often chlorinated. This segment of the subcategory is excluded under Paragraph 8(b)(ii).

The remaining three plants mix calcium hypochlorite process wastewater with chlor-alkali plant wastewater for treatment. EPA proposed to amend the applicability section in the effluent limitations guidelines for chlor-alkali plants to include effluent from the calcium hypochlorite process. Based upon plants sampled in 1979 and 1981, and effluent data provided by those plants, plants that combine these process wastewaters are meeting all existing guidelines and standards for chlor-alkali plants. Relevant data are presented in Table 19-2c (Plant B).

We continue to believe that existing plants that produce both calcium hypochlorite and chlor-alkali can meet the effluent limitations and standards for the chlor-alkali subcategory. However, we believe that because the calcium hypochlorite effluent is controlled by the technology on which the chlor-alkali limitations are based, it is more appropriate to exclude the calcium hypochlorite from national regulation, pursuant to paragraph 8(a)(i) of the Settlement Agreement.

21. Cerium Salts. There are two plants currently producing cerium ("ceric") salts as separate products. Other plants may produce small amounts of cerium salts with other rare

earth metals (see Subcategory No. 63). One of these plants is a direct discharger which produces ceric salts from rare earth hydroxides imported from France (7). The second plant, an indirect discharger, obtains rare earth oxides and treats them with various acids to produce the salts. Little effluent is produced by this process (about 40 gallons per day). Consideration was given to combining this subcategory with rare earth metal salts, but this was rejected because the processes employed in this subcategory are substantially different as are the raw materials used.

Since there are only one direct and one indirect discharger, and since the indirect discharger has such a low flow, the Agency is excluding this subcategory from further regulation development under Paragraph 8(a)(iv) and 8 (b)(ii) of the Settlement Agreement.

22. Chlorosulfonic Acid. No toxic pollutants were detected at treatable levels during screening and verification sampling at one plant of the three plants producing this chemical. Effluent wastewater discharged at this plant was the same as influent water quality. Relevant data are presented in Table 19-2d. This subcategory is excluded under the provisions of Paragraphs 8(a)(iii), 8(a)(iv) and 8(b), because toxic pollutants were not detected at treatable levels during screening and verification sampling, hence the toxic pollutant discharges were too insignificant to justify developing a national regulation.

23. Chromium Oxide (a Chrome Pigment). Chromium oxide is defined as a chrome pigment in the promulgated guidelines for the Chrome Pigments subcategory. The promulgated BPT, BAT, and BCT limitations and NSPS, PSES, and PSNS for the Chrome Pigments Subcategory are at 40 CFR 415.340. Therefore, the Agency is excluding this subcategory from further consideration (Paragraph 8(a)(i)). The current effluent limitations would continue to apply.

24. Chromium Sulfate. There is only one plant producing this chemical, therefore the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

25. Heavy Water (Deuterium Oxide). There are no producers of deuterium oxide (heavy water) in the U.S. today. Therefore the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

26. Hydrated Alumina Silicate Powder. There is one plant currently producing this chemical, and this plant has no

discharge of process wastewater. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

27. Hydrogen Sulfide. There are four plants producing hydrogen sulfide essentially as a by-product. Three of the plants are petroleum refineries and one is an organic chemicals plant. Wastewater for the three plants producing hydrogen sulfide at petroleum refineries is subject to effluent limitations for the Petroleum Refining Point Source Category (40 CFR Part 419). These limitations are applicable to all discharges from any facility producing petroleum products by the use of topping, catalytic reforming, cracking, petrochemical operations, and lube oil manufacturing whether or not the facility includes any process in addition to those listed above. There is only one other plant. Therefore, the Agency is excluding this subcategory from national regulation development under Paragraph 8(a)(i), 8(a)(iv), and 8(b).

28. Hydrophosphites. This chemical is no longer produced in this country. Therefore, the Agency is excluding this subcategory under the provisions of Paragraphs 8(a)(iv) and 8(b)(ii) because there are no known producers.

29. Indium Chloride. There are three plants in this subcategory but only one has a discharge. All plants produce small quantities as a specialty product. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) because there is only one discharger.

30. Industrial Gases. Specific industrial gases not addressed elsewhere are the "rare" or "inert" gases produced in conjunction with oxygen and nitrogen from liquefaction of air (e.g., neon and argon). In Phase I, oxygen and nitrogen were excluded under Paragraph 8(a)(iv) because the amount and toxicity of each pollutant observed in samples collected from plants in the subcategory did not justify developing national regulations (see the Phase I Development Document, p. 806). Since the inert gases are produced simultaneously with oxygen and nitrogen from the same liquid air, and the wastewaters were included in the samples collected in Phase I, the Agency is excluding these products also under the provisions of Paragraph 8(a)(iv) and 8(b)(ii).

31. Inorganic Acids (except nitric and phosphoric acid). The only common inorganic acids not addressed elsewhere are:

a. Hydrobromic Acid - There is no discharge of process wastewater from production of this chemical.

b. Hydriodic Acid - There is no discharge of process wastewater from production of this chemical.

Since there is no process wastewater discharged from this subcategory, the Agency is excluding it under the provisions of Paragraphs 8(a)(iv) and 8(b)(ii).

32. Iodides. Specific iodides not addressed elsewhere are:

a. Calcium Iodide - There is only one plant producing this chemical and that plant has no discharge of process wastewater from calcium iodide production.

b. Lithium Iodide - There are two plants producing this chemical, but neither has a discharge of lithium iodide process wastewater.

c. Sodium Iodide - There are two plants producing this chemical in bulk form, but only one has a discharge. That plant discharges an estimated 1000 gallons per year directly to a receiving stream.

Since there is only one discharger, with a discharge of only 1000 gallons per year, this subcategory is excluded under the provisions of Paragraphs 8(a)(iv) and 8(b)(ii).

33. Iron Colors. Iron colors can be broadly subdivided into two groups: those colors based upon various iron oxides (see No. 34-36 below), and those colors, generally blue, based on iron cyanide complexes. The products based upon iron oxides are considered below under iron oxides (iron oxide pigments). There is only one plant (a direct discharger) producing iron cyanide-based pigments. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) because there is only one plant.

34, 35, 36, 48, 67, and 94. Iron Oxide(s) (Iron Oxide Pigments). These subcategories include the Iron Oxides (Black, Yellow, Red, and Magnetic) and the Ochers, Siennas, and Umbers Subcategories. Four plants, one direct and three indirect dischargers, produce iron oxide pigments by an inorganic chemical process. One other plant produces iron oxide pigments by an organic chemical process. Most iron oxide pigments producers use a mechanical (grinding) process. Based upon screening and verification sampling at two [illegible] the four inorganic chemical plants, there are no toxic pollutants at treatable levels discharged from any of these four plants. Relevant data are presented in Table 19-2f. All three indirect dischargers are required by the POTWs to control the nonconventional pollutant iron. All four plants (including the direct discharger) use the same treatment technology to control the discharge of iron, and, based on long-term data from the direct discharger, that technology is the technology the Agency would have chosen as the basis for BAT and PSES. Since the three indirect dischargers are already required to control the discharge of iron using that technology, and since there is only one direct discharger, the Agency is excluding these six subcategories under Paragraphs 8(a)(iv) and 8(b).

37. Lead Arsenate. This chemical is no longer produced in this country and is unlikely to be produced in the future. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) of the Settlement Agreement.

38,39. Lead Dioxide (Red) and Lead Dioxide (Brown). No process wastewater is discharged from any plant producing these products. Therefore, the Agency is excluding these two subcategories under Paragraphs 8(a)(iv) and 8(b)(ii) (no discharging plants).

40. Lead Silicate. See "White Lead Pigments," subcategory number 95.

41. Lithium Compounds. Specific lithium compounds not addressed elsewhere are:

   a. Lithium Chloride - There are three plants, but none discharge process wastewater.

   b. Lithium Fluoride - There are two plants, but the total production is estimated to be less than 4 tons per year. The wastewater discharge flow from such a small production is insignificant.

   The chemicals in this subcategory are excluded under Paragraphs 8(a)(iv) and 8(b) because the discharge of toxic pollutants is insignificant.

42. Magnesium Compounds (Inorganic). Specific magnesium compounds not addressed elsewhere are:

   a. Magnesium Chloride - There are eight plants employing two different processes to obtain this chemical. Four plants derive magnesium chloride from natural brines and return the spent brines to their source. The other four plants produce the product from magnesium hydroxide and hydrochloric acid by a process which generates no wastewater. Hence there are no dischargers.

b. Magnesium Fluoride - This chemical is produced from hydrofluoric acid and magnesium hydroxide on a specialty basis at two plants. The total production is less than ten tons per year, which results in an insignificant discharge.

c. Magnesium Nitrate - There are five plants producing this chemical, however, the two large plants have no discharge of process wastewater from this product. The other three plants (one direct and two indirect dischargers) produce specialty or reagent grades only in small quantities. The total flow is estimated to be less than 20,000 gallons per year.

d. Magnesium Silicate - There are only two plants, and one has no discharge.

e. Magnesium Sulfate - There are five plants producing this chemical, but none of the plants have a discharge.

f. Magnesium Carbonate - There are four plants (three direct and one indirect) producing magnesium carbonate but each uses a different raw material source and production process (ore, by chemical process, from ocean brine, and solution mining). Since each plant uses an entirely different process and raw material source, the identity and quantity of pollutants would be different for each process. Hence, this chemical would require different subcategories each with one plant. The one indirect discharger is estimated to discharge less than 5,000 gallons per year because of its very low production rate.

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b). For magnesium carbonate, two of the four plants are producing small quantities, while all four of the plants produces by a different process.

43. Magnesium Dioxide (Powdered Synthetic). There are eight plants in this subcategory but seven plants do not discharge process wastewater from this product. Therefore, the Agency

is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii), because there is only one discharging plant.

44. Mercury Chloride. There is only one plant producing this chemical. The plant is an indirect discharger and is required by the POTW to control its discharge using an advanced level technology. That technology involves additional treatment beyond that used as the basis for the chlor-alkali BAT limitations and therefore toxic pollutant discharges to the POTW are expected to be insignificant. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b).

45. Mercury Oxides. There is only one plant producing this chemical. That plant is the same plant that produces mercury chloride (product No. 44 above) and combines the wastewaters from both products for treatment. For the reasons presented for excluding mercury chloride, the Agency is excluding this chemical subcategory under Paragraphs 8(a)(iv) and 8(b).

46. Nickel Ammonium Sulfate. There are two plants producing this chemical. One has no discharge of process wastewater from this product. The second produces reagent and specialty grade chemicals along with hundreds of other chemicals in small quantities. All combined wastewater is treated in an advanced level treatment system prior to discharge. Monitoring data confirms the absence of toxic pollutants at treatable levels at this plant. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

47. Nitrous Oxide. There are six plants in this subcategory, all of which are indirect dischargers. Total process wastewater discharge at all six plants is only 30,000 gallons per day. Screening and verification sampling of all the process wastewater sources at two plants showed that no toxic or nonconventional pollutants are discharged at treatable levels in process wastewater from plants in this subcategory. The screening and verification sampling of the final effluent at both plants detected ammonia at excessive levels, but at very low levels in all process wastewater sources contributing to that final effluent. Relevant data are presented in Table 19-2e. At one plant, the water in the discharge trench was so low that the trench had to be dammed to raise the water level so samples could be obtained. The dam was constructed of ceramic clay wrapped in an old burlap sack found at the plant. This could have introduced pollutants into the sample causing the high

values found. The ammonia could not be process related at that plant because all process wastewater sources were sampled and no ammonia was found at treatable levels in those sources. At the second plant, the source of the ammonia is believed to be fugitive ammonium nitrate dust (the raw material for nitrous oxide production). Proper control of dust emissions to the air could correct this problem. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8 b(ii).

48. Ochers (Iron Oxide Pigments). See Iron Oxide Pigments, Subcategories No. 34, 35 and 36.

49. Oleum (Sulfuric Acid). Oleum is sulfuric acid. Sulfuric acid has been excluded from further national BAT regulation in Phase I because no toxic pollutants were found at treatable levels during screening sampling (see the Phase I Development Document, pages 830, 832).

50. Oxidation Catalysts Made from Porcelain. There are no plants producing this material in the U.S. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

51. Perchloric Acid. There is only one plant which produces this chemical. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

52. Peroxides (Inorganic). Specific peroxides not addressed elsewhere are:

    a. Sodium Peroxide - There is only one plant producing this chemical by a dry process. Therefore there is no discharge of process wastewater.

    b. Potassium Peroxide - There are no producers of this chemical in the United States today.

    The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) because there are no discharging facilities.

53. Potash Alum. This subcategory has been addressed under the "Alums" Subcategory, No. 5.

54. Potash Magnesia. There are two plants producing this chemical from ore. These plants are located in an arid area and dispose of all aqueous wastewater in evaporation ponds with no discharge.

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) of the Settlement Agreement.

55. Potassium Aluminum Sulfate. This chemical is "potash alum" which has been addressed under the "Alums" subcategory, No. 5.

56. Potassium Bromide. This subcategory has been addressed under the "Brine Chemicals" subcategory, No. 18.

57. Potassium Carbonate. This chemical is produced at only one plant, a direct discharger. The chemical process generates little wastewater which results from the infrequent washdown of the reactor. Most of that wastewater is recovered and recycled, but some is discharged. The discharge averages less than 10,000 gallons per day.

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) because there is only one plant and the discharge is insignificant.

58. Potassium Chlorate - There is only one producer, a direct discharger. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

59. Potassium Compounds (Inorganic). Specific potassium compounds not addressed elsewhere are:

a. Potassium Fluoride - There are three plants in this subcategory, but only two dischargers, both direct dischargers. One plant produces less than 4.5 kkg/yr (<10,000 lb/yr) of the product and all wastewater from hundreds of chemicals produced at that site is commingled in the plants' advanced wastewater treatment system. The remaining plant has intermittent production and generates less than 0.38 cubic meters per day (<100 gpd) of process wastewater when producing the chemical. The total discharge from both plants is estimated to be less than 5,000 gallons per year.

b. Potassium Bicarbonate - This chemical is produced on a specialty basis (i.e., low production quantities) at two locations. Each plant (one direct and one indirect discharger) makes numerous other reagent and specialty chemicals with all wastewater handled in a common plant treatment system. The total discharge from potassium bicarbonate production from both plants is estimated to be less than 10,000 gallons per year.

c. Potassium Thiocyanate - There is one plant producing this chemical in quantity while two other plants have very low production rates. The process is essentially dry and there are no dischargers.

d. Potassium Silicofluoride - There is one plant producing this chemical but no process wastewater is discharged from this product.

e. Potassium Silicate - No toxic pollutants attributable to potassium silicate production were detected during screening and verification at one plant of three producing the chemical. The process is identical to the process used to produce sodium silicate except for the substitution of potassium hydroxide for sodium hydroxide when the potassium salt is made. Sodium silicate was excluded in Phase I because no toxic pollutants were detected at treatable levels in untreated wastewater at the one plant sampled.

The Agency is excluding all of the above chemical products in this subcategory under Paragraph 8(a)(iv) and 8(b)(ii) of the Settlement Agreement because of low production resulting in little or no discharge and thus insignificant discharges of toxic and nonconventional pollutants.

60. Potassium Cyanide. There are only two plants producing this chemical at present. One achieves zero discharge by total recycle, and the second plant discharges process wastewater to a POTW after treating for cyanide removal by alkaline chlorination.

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b), because the one discharger is required by the POTW to utilize advanced treatment for pretreating wastewater before discharge to the POTW.

61. Potassium Hypochlorate. This chemical is no longer produced in the United States. The Agency is excluding this subcategory under the provisions of Paragraphs 8(a)(iv) and 8(b)(ii).

62. Potassium Nitrate and Sulfate. The potassium sulfate subcategory was excluded in Phase I BAT development because the promulgated BPT and BAT for the potassium sulfate subcategory required that plants achieve no discharge of process wastewater pollutants. There is one potassium nitrate plant in the U.S. This plant is a direct discharger.

Because equal or more stringent effluent limitations have been promulgated for potassium sulfate manufacturing, and because there is only one potassium nitrate producer, the Agency is excluding the potassium nitrate and sulfate subcategory from further regulation development under the provisions of Paragraphs 8(a)(i), and 8(a)(iv), and 8(b)(ii).

63. Rare Earth Metals Salts. There are five known producers of rare earth metal salts in the U.S. (Cerium or ceric salts are discussed above in Subcategory No. 21). Three of the five plants achieve zero discharge, and there is one direct discharger and one indirect discharger in the subcategory (7). The direct discharger produces less than 4.5 kkg per year (<10,000 lb/yr) and combines wastewater from many chemical products together for treatment. The indirect discharger produces rare earth metal salts from an ore concentrate which contains thorium, which is an entirely different process. That plant is required by the POTW to control its discharge to the POTW. Thorium and related materials that may be in the wastewater are source, by-product, or special nuclear material, as these terms are defined at 10 CFR §20.3(a), (3), (15), and (16). As such, the wastewater discharges of these materials are controlled by the Nuclear Regulatory Commission. The Supreme Court decided, in Train v. Colorado PIRG, 426 U.S.1 (1976), that these materials, at least when regulated by the NRC, are not "pollutants" under the Clean Water Act.

Accordingly, the Agency is excluding this subcategory from further regulatory development under Paragraphs 8(a)(iv) and 8(b).

64. Reagent Grade Chemicals. Reagent grade chemicals are a particular grade or quality (purity) of chemical. The term can apply to any chemical. All the individual chemical products included within the inorganic chemicals manufacturing point source category could be produced as a reagent grade chemical. All of the regulations and exclusions promulgated in Phase I, and all of the regulations and exclusions promulgated in Phase II included the production of each product (within a subcategory) in reagent grade quality as well as other (lower purity) grades. Hence, each reagent grade chemical has been addressed separately as the individual chemical. Therefore, the Agency is excluding this subcategory under the provisions of Paragraph 8(a)(i) (for chemicals included under regulated subcategories) and 8(a)(iv) (for chemicals included under subcategories that have been excluded).

65. Salts of Rare Earth Metals. This subcategory is identical to No. 63 above.

66. Satin White Pigment. This chemical product is produced at only one plant. Therefore the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

67. Siennas. (See Iron Oxide Pigments, No. 34-36).

68. Silica, Amorphous. There are seven plants in the subcategory. Screening and verification sampling at three of the seven plants found no toxic pollutants at treatable levels at any of the three plants. Relevant data are presented in Table 19-2g (Plants A, B and C). This subcategory is excluded under Paragraphs 8(a)(iii), 8(a)(iv) and 8(b)(ii) (low loading).

69. Silica Gel. There are three plants in this subcategory. Screening and verification sampling at one of these plants found no treatable levels of toxic or nonconventional pollutants in effluent from that plant. Relevant data are presented in Table 19-2h. This subcategory is excluded under Paragraphs 8(a)(iii), 3(a)(iv), and 8(b)(ii).

70. Silver Bromide. This chemical is produced in very small quantities for research or other highly specialized uses. There is only one discharger in this subcategory. That one plant discharges to a POTW. Minimal wastewater is expected from such small production volumes and no significant pollutant loads are anticipated. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b).

71. Silver Carbonate. This chemical is produced in very small quantities for research or other highly specialized uses. There is only one discharger in this subcategory. That one plant discharges to a POTW. Minimal wastewater is expected from such small production volumes and no significant pollutant loads are anticipated. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b).

72. Silver Chloride. This chemical is produced in very small quantities for research or other highly specialized uses. There is only one discharger in this subcategory. That one plant discharges to a POTW. Minimal wastewater is expected from such small production volumes and no significant pollutant loads are anticipated. Therefore, the Agency is

excluding this subcategory under Paragraphs 8(a)(iv) and 8(b).

73. Silver Cyanide. There are two plants which manufacture this chemical. Both plants discharge to a POTW. One plant's discharge is less than 1.9 cubic meters per day (<500 gpd) and treats the discharge with an advanced wastewater treatment system for silver recovery and to comply with the POTW's pretreatment requirements. The second plant treats all process wastewater with a two stage ion-exchange system for silver recovery, and to comply with the POTW's pretreatment requirements. Since both plants must comply with the POTW's pretreatment requirements, and since the value of the recovered silver offsets most or all of the cost of the treatment sytems, the plants are unlikely to cease operating the treatment systems. Therefore, the Agency is excluding the subcategory under Paragraphs 8(a)(iv) and 8(b).

74. Silver Iodide. This chemical is produced in very small quantities for research or other highly specialized uses. There is only one discharger in this subcategory. That one plant discharges to a POTW. Minimal wastewater is expected from such small production volumes and no significant pollutant loads are anticipated. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b).

75. Silver Nitrate. There are three plants in this subcategory. Screening and verification sampling at the largest of these plants found no toxic or nonconventional pollutants at treatable levels in the treated wastewater from this process. The wastewater discharged at that plant was in compliance with existing BPT effluent limitations. PSES has also been promulgated for this subcategory. 40 CFR 415.530 lists the applicable discharge limitations and standards for the silver nitrate subcategory.

The Agency is excluding this subcategory from further regulatory development under Paragraph 8(a)(iv) and 8(b).

76. Silver Oxide. There are currently two plants producing this chemical. One is a direct discharger, and one is an indirect discharger. The indirect discharger treats process wastewater in a two-stage ion exchange system before discharge to a POTW. The direct discharger produces only research quantities of silver oxide (only 2 kg (4.4 lb.) in 1981). All wastewater from this process and other plant process water is treated in a lime precipitation-alum

coagulation treatment system before discharge. Process wastewater volume discharged is negligible.

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b).

Note: The Agency considered combining all the silver product subcategories (No.'s 70 to 76) into a silver compounds subcategory. However, silver nitrate is soluble in water whereas the other six products are insoluble, so that the production process, raw materials, expected pollutants and unit flows are significantly different for silver nitrate production compared to the other six products. Therefore, the combined subcategory would have to have two segments, which does not appear to provide significant regulatory simplification. The Agency also considered combining six products (No.'s 70, 71, 72, 73, 74, and 76) into one subcategory. There are six plants which manufacture one or more of those products, but only three (one direct and two indirect) dischargers. The direct discharger produces only a few pounds of silver compounds each year, and consequently generates minimal wastewater. That minimal wastewater is treated with an advanced level treatment technology for silver recovery. The two indirect dischargers use advanced level treatment systems for silver recovery and to comply with the pretreatment requirements established by the POTWs. Accordingly, the Agency has not combined the silver products into a new silver comppounds subcategory, because that new subcategory would also have been excluded under Paragraph's 8(a)(iv) and 8(b).

77. Soda Alum. This subcategory has been addressed under the "Alums" Subcategory, No. 5.

78. Sodium Antimonate. This product is generated at only two sites by a process releasing no wastewater. Therefore, the Agency is excluding this subcategory from national effluent limitations development under Paragraphs 8(a)(iv) and 8(b)(ii).

79. Sodium Compounds (Inorganic). Specific sodium compounds not addressed elsewhere are:

    a. Sodium Molybdate - There are two plants producing this chemical. One has no discharge, while the second produces research quantities and is a direct discharger. The total flow from the process at the second facility is estimated to be less than 10,000 gallons per year. The second facility produces a large number of different chemicals of many types on an intermittent basis. All plant process wastewater is treated in an advanced treatment system.

b. Sodium Perborate - There is one plant, a direct discharger, producing this chemical.

c. Sodium Perchlorate - There are only two plants producing this chemical and neither has a discharge.

d. Sodium Stannate - Three plants (two direct dischargers and one indirect discharger) produce this chemical on a specialty basis along with many other chemicals. Production quantities at each plant are very low. The total flow from all three plants is estimated to be less than 10,000 gallons per year.

e. Sodium Thiocyanate - There are three plants producing this chemical but none of the plants discharge process wastewater.

f. Sodium Tungstate - There are two plants producing this chemical, but one plant achieves no discharge of process wastewater. The remaining plant discharges less than 1.9 cubic meters per day (<500 gpd) of process wastewater from this product.

The Agency is excluding the above chemical products under Paragraphs 8(a)(iv) and 8(b)(ii) because the volume of wastewater discharged is insignificant.

80. Sodium Cyanide. There are two plants producing this chemical in the U.S. today. One plant achieves zero discharge while the second plant discharges process wastewater together with other process water through the plant treatment system and then to a POTW. Alkaline chlorination is used at this plant to destroy cyanide before discharge. The discharge is treated in compliance with the POTW's pretreatment requirements, consequently the plant is unlikely to cease operating the treatment system.

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b).

This plant is also the only potassium cyanide producer with a discharge. Therefore, the Agency did not combine the potassium cyanide and sodium cyanide subcategories, since there is only one discharger.

81. Sodium Hydrosulfite (Zinc Process). There is one plant producing this chemical by the zinc process. This plant achieves no discharge of process wastewater from this product. Therefore, this subcategory is excluded under Paragraph 8(a)(iv).

82. Sodium Silicofluoride. This chemical is produced as a by-product of wet process phosphoric acid production at six fertilizer plants and by one plant which does not produce wet process phosphoric acid. At phosphate fertilizer plants there is no discharge of process wastewater from the production of sodium silicofluoride. The one plant which does not produce sodium silicofluoride as a by-product of wet process phosphoric acid production uses a different production process to manufacture sodium silicofluoride. Thus there is only one discharger in this subcategory.

Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

83. Stannic and Stannous Chloride. There are three plants which produce tin chlorides, but only two have a discharge. Both are direct dischargers. Both plants produce the products intermittantly at low production rates. The total discharge is estimated to be less than 5,000 gallons per year. Therefore, no significant pollutant loads are expected from these sources, and the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

84. Strontium Carbonate. There are five plants which produce strontium carbonate but only three plants have a discharge of process wastewater (two direct dischargers and one indirect discharger). All three dischargers also produce barium carbonate and combine the wastewaters from both products for treatment and discharge. One of the three plants was sampled in Phase I and no toxic pollutants were detected. Therefore, the Agency is excluding this subcategory under the Paragraphs 8(a)(iv) and 8(b)(ii).

85. Strontium Nitrate. There are four plants producing this chemical. One of the producers achieves no discharge of process wastewater. One of the two indirect dischargers discharges to a POTW but the flow is low (less than 0.4 cubic meters per day (<100 gpd). The other indirect discharger produces the chemical in small quantities and is estimated to discharge less than 5,000 gallons per year to POTW. The remaining plant is a direct discharger which also produces the chemical in small quantities, with an estimated discharge of about 5,000 gallons per year.

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

86. Sulfide and Sulfites. All specific sulfides and sulfites are addressed elsewhere under the metal sulfide or sulfite such as sodium hydrosulfite, sodium sulfite, barium sulfide, sodium hydrosulfide. Regulations have been promulgated for sodium sulfite; sodium hydrosulfite, barium sulfide, and sodium hydrosulfide have been excluded. Therefore the Agency is excluding this subcategory under Paragraphs 8(a)(i), 8(a)(iv) and 8(b)(ii).

87. Sulfocyanides (Thiocyanates). All sulfocyanides or thiocyanates are addressed elsewhere (such as No. 59 (Potassium Thiocyanate) or No. 79(e) (Sodium Thiocyanate)). There are no dischargers. Therefore, the Agency is excluding the sulfocyanides (thiocyanates) subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

88. Sulfur (Recovered or Refined Including Sour Natural Gas). This chemical is produced (a) at petroleum refineries from crude petroleum, and (b) as part of the process of removing hydrogen sulfide from sour natural gas. The national BAT regulations for the Petroleum Refining Industry address the total wastewater discharge from petroleum refineries, including any wastewater from sulfur production (40 CFR 419). Accordingly, the Agency is excluding this segment of the Sulfur subcategory under Paragraph 8(a)(i) because it is regulated under another industrial category. There is no wastewater discharge from the production of sulfur from sour natural gas, and therefore the Agency is excluding this segment under Paragraph 8(a)(iv) and 8(b)(ii).

89. Sulfur Chloride. Specific sulfur chlorides considered were:

a. Sulfur Monochloride - There are three plants, but only one has a discharge.

b. Sulfur Dichloride - There are two plants, but only one has a discharge.

c. Thionyl Chloride - There are two plants, but only one has a discharge.

d. Sulfuryl Chloride - There are only two plants, but only one has a discharge.

The one discharger produces all four chemicals. Therefore, the Agency is excluding this subcategory under Paragraphs 8 (a)(iv) and 8(b)(ii) because there is only one discharger in the subcategory.

90. Sulfur Hexafluoride. There are two plants in this subcategory, one a direct discharger and the other does not discharge from this process. The direct discharger has only a small volume of process wastewater (1.5 cubic meters per day (<400 gpd)).

The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) because there is only one discharger in the subcategory.

91. Thiocyanates. (See Subcategory No. 59 (c), 79 (f) and 87).

92. Tin Compounds. Most tin compounds not addressed elsewhere are produced, if at all, only infrequently as low volume special order or research products. The only tin compound not addressed elsewhere which is produced in quantity is tin fluoborate. There are four plants producing tin fluoborate. However, only one plant has a discharge of 19 cubic meters per year (5000 gallons per year). This flow is too insignificant to justify developing a national regulation and therefore the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii). Screening and verification sampling data for the one discharger are presented in Table 19-2i.

93. Ultramarine Pigments. These substances are not produced in the U.S. at present. Therefore, the Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii).

94. Umbers. This subcategory has been addressed under Iron Oxides - see subcategory No. 34.

95. White Lead Pigments. The white lead pigments subcategory includes the production of lead carbonate, lead silicate (subcategory No. 40), and lead sulfate. There are three plants producing any of these products, one of which is a direct discharger and the other two are indirect dischargers. Both indirect dischargers are required by the POTWs to treat the wastewater before discharge to the POTWs. One plant must comply with the POTW's limitation for lead of 0.5 mg/l (long-term average). The second plant has installed lime precipitation, clarification, and filtration technology to comply with the other POTW's pretreatment requirements. That technology is the technology the Agency believes it would have used as the basis for any PSES (or BAT) regulations. Since the plants are required by the

POTWs to pretreat, the plants are unlikely to cease operating the treatment technologies. Accordingly, a PSES is not needed. Since there is only one direct discharger, and both indirect dischargers must comply with pretreatment requirements imposed by the POTWs, the Agency is excluding the white lead pigments and lead silicate subcategories under Paragraphs 8(a)(iv) and 8(b).

96. Whiting (Calcium Carbonate). Whiting is another name for Calcium Carbonate. The promulgated guidelines for the Calcium Carbonate Subcategory are at 40 CFR 415.300. Calcium carbonate has been excluded from futher national BAT regulation development in Phase I because no toxic pollutants were found at treatable levels during screening sampling. (See the Phase I Development Document, pg. 793.). Therefore, the Agency is excluding this subcategory from further national regulation development under the provisions of Paragraphs 8(a)(iv) and 8(b)(ii).

97. Zinc Sulfide. There are two plants in this subcategory, one of which has no discharge. The single discharger makes many specialty chemicals in small quantities primarily for captive consumption. The discharge of zinc sulfide process wastewater is less than 500 gallons per day. The Agency is excluding this subcategory under Paragraphs 8(a)(iv) and 8(b)(ii) because there is only one discharging plant in the subcategory.

Radioactive Materials

General. Ten of the subcategories in Phase II involve the production of products which are radioactive. For convenience in the regulatory review, these ten subcategories have been grouped together. Those ten subcategories are:

98. Cobalt 60

99. Fissionable Materials

100. Isotopes, Radioactive

101. Luminous Compounds (Radium)

102. Nuclear Cores, Inorganic

103. Nuclear Fuel Reactor Cores, Inorganic

104. Nuclear Fuel Scrap Reprocessing

105. Radium Chloride

106. Radium Luminous Compounds

107. Uranium Slugs, Radioactive

In many cases two or more of the ten subcategories refer to the same or similar products. To facilitate the Agency's review, the similar subcategories were addressed together, as follows:

(a) Cobalt 60 and isotopes, radioactive, since cobalt 60 is a radioactive isotope.

(b) Luminous compounds (radium), radium chloride, and radium luminous compounds, since all three subcategories involve radium.

(c) Fissionable materials, nuclear cores (inorganic), nuclear fuel reactor cores (inorganic), and uranium slugs (radioactive), since all four subcategories refer to the production of the fissionable uranium slugs used in nuclear reactors.

(d) Nuclear fuel scrap reprocessing.

The rationale for the Agency's actions for each group of subcategories is presented below.

A. Cobalt 60 and other radioactive isotopes are produced in nuclear reactors by inserting the non-radioactive precurser (such as a non-radioactive isotope of cobalt) into the reactor, where it is bombarded by neutrons released in the reactor. The cobalt 60 (or other radioactive isotope) produced is removed from the reactor and used as produced. There is no water used in producing the radioactive isotopes and no wastewater is generated or discharged. Therefore, the Agency is excluding the cobalt 60 and isotopes, radioactive subcategories from regulation under Paragraph 8(a)(iv) because there are no dischargers.

B. No radium chloride or radium luminous compounds (luminous compounds, radium) are produced in this country nor have any been produced for over 25 years. Hence, the Agency is excluding the radium chloride, radium luminous compounds, and luminous compounds, radium subcategories from regulation under Paragraph 8(a)(iv) because there are no producers.

C. Fissionable materials production involves the production of the uranium or uranium oxide slugs used as the fuel in nuclear reactors. The fuel is loaded into the reactor in rods. Since, strictly speaking, the nuclear core is an assembly of fuel rods, moderators, and supporting elements, and the assembling of the core is a construction process, the Agency has interpreted the nuclear cores (inorganic), and nuclear fuel reactor cores (inorganic) subcategories to mean the production of the fissionable uranium slugs used in the core fuel rods, as that is the only chemical process.

Fissionable materials (nuclear cores, nuclear fuel reactor cores, uranium slugs) production is conducted in this country only under license issued by the Nuclear Regulatory Commission (NRC). The license controls all aspects of the production of fissionable materials including wastewater discharges. Any materials in the wastewater are source material, by-product material, or special nuclear material, as these terms are defined in the Atomic Energy Act of 1954, as amended. The Supreme Court decided in Train v. Colorado PIRG, 426 U.S.1. (1976) that these materials, at least when regulated by the NRC, are not "pollutants" under the Clean Water Act.

D. Spent nuclear fuel may be reprocessed to recover useful fissionable materials that may remain in the spent fuel or, in the case of plutonium 239, have been produced during the "burn" cycle. All facilities engaged in this process operate under licenses issued by the NRC. The licenses control all aspects of the reprocessing, including wastewater discharges. Any materials in the wastewater are source material, by-product material, or special nuclear material, as these terms are defined in the Atomic Energy Act of 1954, as amended. The Supreme Court decided, in Train v. Colorado PIRG, 426 U.S.1. (1976) that these materials, at least when regulated by the NRC, are not "pollutants" under the Clean Water Act.

Table 19-2. SUMMARY OF TOXIC AND NON-CONVENTIONAL POLLUTANT DATA FOR SCREENING/VERFICATION SAMPLING (Table 19-2a, AMMONIUM THIOSULFATE).

SUBCATEGORY: 10 - Ammonium Thiosulfate

	Concentration (mg/l)	
Pollutant	Plant A*	Plant B
Sb	0.88	0.32
As	0.004	0
Be	0.008	0
Cd	0.084	0.016**
Cr	0.153	0.071
Cu	2.0	0.01
Pb	3.6	0.44
Hg	0.006	0
Ni	0.38	0
Sl	0.018	0
Ag	0.002	0
Tl	0.121	0.13
Zn	1.3	0
NH_3	7300	Not Analyzed
Ethylbenzene	0.019	-
Tolune	0.021	-
2,4 Dinitrophenol	0.351	-
4,6 Dinitro-o-cresol	0.054	-
Bis (2-ethylhexyl)phthalate	0.033	-
Thiosulfate	23,000	1

* Samples may have been contaminated by contact with sealing compound on new floor. Total flow averaged 150 gallons per day.

** Two samples only. Analysis for cadmium in third sample erroneous, as analysis of the blank for that sample showed high cadmium result.

Table 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERIFICATION SAMPLING (Table 19-2 b, BRINE CHEMICALS)

SUBCATEGORY: 18 - Brine Chemicals

Pollutant	Concentration (mg/l) Plant A
Sb	0.003
As	0.0002
Be	0.0002
Cd	0.057
Cr	0.091
Cu	0.13
Pb	0.079
Hg	0.0003
Ni	0.052
Se	0.014
Ag	0.055
Tl	0.008
Zn	0.55

Flow averaged 700 gallons per day.

Table 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERIFICATION SAMPLING (Table 19-2 c, CALCIUM HYPOCHLORITE).

SUBCATEGORY: 20 - Calcium Hypochlorite

Pollutant	Plant A	Plant B
Sb	0.1	4.1
As	0.004	0.002
Be	0.001	0.011
Cd	0.006	0.15
Cr	0.039	0.11
Cu	0.041	0.17
Pb	0.14	0.27
Hg	0.002	0.01
Ni	0.015	0.6
Se	0.004	0.007
Ag	0.0003	0.014
Tl	0.002	1.1
Zn	0.085	0.37
Chloroform	0.090	0.17
Methylene Chloride	0.014	1.1
Dichlorobromomethane	0.025	ND
Chlorodibromomethane	0.041	0.0007

Table 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERIFICATION SAMPLING (Table 19-2 d, CHLOROSULFONIC ACID).

Subcategory: 22 - Chlorosulfonic Acid

	Concentration (mg/l)
Pollutant	Plant A
Sb	0.067
As	0.017
Be	0.0011
Cd	0.0
Cr	0.0036
Cu	0.0
Pb	0.0
Hg	0.0
Ni	0.022
Se	0.0
Ag	0.0
Tl	0.01
Zn	0.0067
Chloroform	0.017
Methylene Chloride	0.014
Di-n-octyl phthalate	0.011

Table 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERIFICATION SAMPLING (TABLE 19-2 e, NITROUS OXIDE).

SUBCATEGORY: 47- Nitrous Oxide

	Concentration (mg/l)	
Pollutant	Plant A	Plant B
Sb	0.06	0.008
As	0.01	0.004
Be	0.002	0.001
Cd	0.002	0.009
Cr	0.24	0.060
Cu	0.021	0.075
Pb	0.007	0.061
Hg	0.002	0.005
Ni	0.035	0.009
Se	0.015	0.003
Ag	0.002	0.0007
Tl	0.01	0.003
Zn	0.08	0.015
NH_3-N*	360.	3400.

* See Text.

Table 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERIFICATION SAMPLING (Table 19-2 f, IRON OXIDE PIGMENTS).

SUBCATEGORY: 34,35,36,48,67,94 - Iron Oxide Pigments

Pollutant	Concentration (mg/l) Plant A*	Plant B	Plant C**
Sb	0.55	0.13	
As	0.005	0.002	
Be	0.005	0.002	
Cd	0.036	0.002	
Cr	0.22	0.038	0.02
Cu	0.12	0.018	0.045
Pb	0.39	0.13	
Hg	0.001	0.003	
Ni	0.74	0.21	0.04
Se	0.015	0.009	
Ag	0.008	0.044	
Tl	0.14	0.084	
Zn	0.65	0.015	0.04
Fe	83	Not Analyzed	9.3
Methylene Chloride	Not Analyzed	0.015	

* Treatment system not functioning optimally. Effluent not in compliance with POTW's requirements.

** Long-term treatment system performance data.

TABLE 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERFICATION SAMPLING (Table 19-2 g, SILICA, AMORPHOUS).

SUBCATEGORY: 68 - Silica, Amorphous

Pollutant	Plant A*	Plant B	Plant C
Sb	0.008	0.075	0.12
As	0.009	0.025	0.0025
Be	0.0005	0.002	0.005
Cd	0.011	0.011	0.016
Cr	0.09	0.017	0.015
Cu	0.018	0.011	0.013
Pb	0.01	0.10	0.20
Hg	0.002	0.003	0.001
Ni	0.17	0.037	0.12
Se	0.007	0.046	0.015
Ag	0.007	0.0012	0.01
Tl	0.003	0.006	0.007
Zn	0.16	0.086	0.031
Chloroform	0.192	ND	ND
Methylene Chloride	0.065	ND	0.026
Methyl Chloride	0.548	ND	ND
Dichlorobromomethane	0.015	ND	0.028
2,4 Dinitrophenol	0.064	ND	ND
Di-n-octyl phthalate	0.012	ND	ND
1,1,1 - Trichloroethane	ND	ND	0.086

* Toxic organic pollutants from organic chemical process at same site.

Table 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERIFICATION SAMPLING (Table 19-2 h, SILICA GEL).

SUBCATEGORY: 69 - Silica Gel

Pollutant	Concentration (mg/l) Plant A
Sb	0.067
As	0.023
Be	0.002
Cd	0.005
Cr	0.024
Cu	0.024
Pb	0.030
Hg	0.0
Ni	0.038
Se	0.35
Ag	0.015
Tl	0.12
Zn	0.048
Chloroform	0.040
Methylene Chloride	0.015

TABLE 19-2. SUMMARY OF TOXIC AND NONCONVENTIONAL POLLUTANT DATA FOR SCREENING/VERIFICATION SAMPLING (Table 19-2 i, TIN COMPOUNDS).

SUBCATEGORY: 92 - Tin Compounds (Tin Fluoborate)

	Concentration (mg/l)
Pollutant	Plant A
Sb	0.008
As	0.016
Be	0.005
Cd	0.006
Cr	0.007
Cu	0.17
Pb	0.12
Hg	0.0005
Ni	0.22
Se	0.005
Ag	0.0004
Tl	0.045
Zn	0.12
Phenol	0.045
Butyl Benzyl Phthalate	0.043

SECTION 19

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Appendix A

Analysis of Long-Term Effluent Monitoring Data
Phase II

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Treatment Technology Abbreviations Used:

Eq = Equalization

Neut = Neutralization

Neut (2) = Two stage neutralization, if used in sequence

FL(m) = Filtration with multi-media

FL(s) = Filtration with sand filter

FL(p) = Filtration with filter press

FL(u) = Filtration-method unknown

CL = Clarifier

S = Sulfide addition

Sd = Sedimentation (basin, pond, lagoon)

RCL = Recycle

pH = pH adjustment

Floc = Flocculant addition

Act. Sludge = Biological activated sludge

AR = Aeration

Cr-Red = Hexavalent chromium reduction

Pcp = Alkaline precipitation

CADMIUM PIGMENTS AND SALTS

TABLE A-1.1 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F101
Subcategory(ies): Cadmium Pigments and Salts
Other Products: Other Pigments
Discharge Status: Indirect
Monitoring Period: January, 1980
Treatment Technology: None

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
pH	Once	Daily	1	N/A	10.21	N/A	N/A	N/A	N/A
TSS	Once	Daily	1	N/A	301	N/A	N/A	N/A	N/A
Cd	Once	Daily	1	N/A	83.88	N/A	N/A	N/A	N/A
Fe	Once	Daily	1	N/A	1.86	N/A	N/A	N/A	N/A
Se	Once	Daily	1	N/A	5.014	N/A	N/A	N/A	N/A
Zn	Once	Daily	1	N/A	16.80	N/A	N/A	N/A	N/A
NH_3-N	Once	Daily	1	N/A	7.01	N/A	N/A	N/A	N/A
Sulfide	Once	Daily	1	N/A	11.0	N/A	N/A	N/A	N/A

N/A = Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.2 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F102
Subcategory(ies):	Cadmium Pigments and Salts
Other Products:	Other Inorganic Chemicals
Discharge Status:	Indirect
Monitoring Period:	July 21, 1982 to August 5, 1982
Treatment Technology:	Eq, Pcp, Floc, Sd, Cr-Red, FL(S), pH

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd (Total)	1/day (1)	Monthly	2	0.05	0.07	0.09	0.40	1.66	0.12
		Daily	12	0.02	0.065	0.16	0.66	3.39	0.22
Cd (Dis)	1/day (1)	Monthly	2	0.019	0.027	0.035	0.42	1.69	0.05
		Daily	12	0.01	0.024	0.08	0.83	4.16	0.10

Reported on 7/21, 22, 23 and 7/26 to 7/30/80 and 8/2 to 8/5/80

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 1.3 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F110
Subcategory(ies): Cadmium Salts and Pigments
Other Products: Other Inorganic Chemicals and Metals
Discharge Status: Zero
Monitoring Period: August, 1978 to November, 1978
Treatment Technology: Pcp, Sd, RCL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd	Not Available	Not Available	N/A	N/A	<0.1	N/A	N/A	N/A	N/A

N/A = Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.4 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F117
Subcategory(ies): Cadmium, Cobalt and Nickel Salts
Other Products: Numerous Catalysts
Discharge Status: Direct
Monitoring Period: January, 1983
Treatment Technology: Cadmium and Cobalt Salts Wastewater Treatment: Pcp, FL(p)

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
pH	Grab Basis	Daily	1	N/A	6.81	N/A	N/A	N/A	N/A
TSS	Grab Basis	Daily	1	N/A	1.2	N/A	N/A	N/A	N/A
Cd	Grab Basis	Daily	1	N/A	0.05	N/A	N/A	N/A	N/A
Co	Grab Basis	Daily	1	N/A	0.09	N/A	N/A	N/A	N/A
Pb	Grab Basis	Daily	1	N/A	0.002	N/A	N/A	N/A	N/A

N/A - Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F119
Subcategory(ies):	Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products:	Numerous Organic & Inorganic Chemicals
Discharge Status:	Indirect
Monitoring Period:	December, 1978 to June, 1980
Treatment Technology:	Neut, Floc, CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd	Daily for 1 week per quarter	Monthly	6	0.03	0.11	0.24	0.89	2.46	0.27
		Daily	30	0.02	0.11	1.08	1.82	8.05	0.89
Cu	Daily for 1 week per quarter	Monthly	6	3.11	5.16	7.1	0.28	1.46	7.5
		Daily	30	0.069	5.15	14.9	0.68	3.48	17.9
Cr	Daily for 1 week per quarter	Monthly	6	2.31	3.76	5.74	0.36	1.59	6.0
		Daily	30	0.65	3.76	11.4	0.72	3.66	13.8
Ni	Daily for 1 week per quarter	Monthly	6	0.63	1.6	3.8	0.69	2.13	3.4
		Daily	30	0.35	1.6	5.7	0.73	3.70	5.9
Zn	Daily for 1 week per quarter	Monthly	6	0.038	0.31	0.68	0.76	2.25	0.70
		Daily	30	0.02	0.31	1.26	1.12	5.44	1.69
CN(A)	Daily for 1 week per quarter	Monthly	5	<0.001	<0.001	0.001	0.00	1.00	<0.001
		Daily	19	<0.001	<0.001	0.001	0.00	1.00	<0.001

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS (Cont.)

Facility Code:	F119 (Cont.)
Subcategory(ies):	Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products:	Numerous Organic & Inorganic Chemicals
Discharge Status:	Indirect
Monitoring Period:	December 1978 to June 1980
Treatment Technology:	Neut, Floc, CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN(T)	Daily for 1 week per quarter	Monthly	5	0.001	0.09	0.38	1.82	3.98	0.36
		Daily	20	<0.001	0.08	1.28	3.54	11.7	0.94

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.6 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F124
Subcategory(ies):	Cadmium, Cobalt and Nickel Salts
Other Products:	Other Organic and Inorganic Chemicals
Discharge Status:	Direct (001)
Monitoring Period:	January 2, 1981 to February 28, 1983
Treatment Technology:	Eq, Floc, Pcp, CL, FL(s), pH, Sd

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics (1)					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Co	1/Day	Monthly	26	0.50	0.97	1.70	0.27	1.44	1.4
		Daily	657	0.008	0.97	7.7	0.74	3.75	3.6
Ni	1/Day	Monthly	26	0.39	0.69	1.14	0.32	1.52	1.0
		Daily	657	0.012	0.69	10.4	0.98	4.83	3.3
Cd	1/Day	Monthly	26	0.032	0.063	0.17	0.47	1.78	0.11
		Daily	657	0.007	0.063	0.59	1.12	5.45	0.34

(1) Effluent concentrations reported here were flow proportioned to account for commingling with non-contact cooling water before discharge.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.7 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F125
Subcategory(ies):	Cadmium and Nickel Salts and Zinc Chloride
Other Products:	Inorganic Chemicals
Discharge Status:	Direct
Monitoring Period:	January, 1981 to January, 1983
Treatment Technology:	Pcp, CL, Sd

Parameter(1) (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics No.	Min.	Avg.	Max.	CV	Variability Factor	Performance Standard (P)
TSS	1/week	Monthly	24	4	8.7	18.2	0.41	1.67	14.5
Cd	1/week	Monthly	24	All values reported as "Not Detected"					
Co	1/week	Monthly	25	All values reported as "Not Detected"					
Cu(2)	1/week	Monthly	11	0.055	0.093	0.14	0.25	1.41	0.13
Ni	1/week	Monthly	24	All values reported as "Not Detected", except 7/82 when the Avg. = 0.04 mg/l and the Max = 0.10 mg/l					
Pb	1/week	Monthly	24	All values reported as "Not Detected"					
Zn	1/week	Monthly	24	0.010	0.15	0.32	0.51	1.84	0.28

(1) Mn is also monitored. However Mn was reported as "Not Detected" throughout the period.

(2) Copper was detected in the wastewater effluent only one month during the period prior to 3/82. At this time a change occurred in the process, resulting in copper detection every month. Therefore the period considered in this analysis was 3/82 to 1/83.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.8 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F128

Subcategory(ies): Cadmium Pigments and Salts

Other Products: Wide Variety of Organic and Inorganic Pigments

Discharge Status: Direct

Monitoring Period: January 1979 to December 1980

Treatment Technology: Pcp, FL(u), (Cadmium Recovery), Eq, Cr-Red, Neut, Sd, FL(m)

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd	1/Week	Monthly	24	0.005	0.076	0.216	0.62	2.02	0.15
		Daily	93	0.0049	0.088	0.54	1.25	5.99	0.53
Hg	1/Week	Monthly	24	0.0001	0.0028	0.0035	2.39	4.92	0.014
		Daily	98	0.00004	0.0027	0.13	4.84	13.1	0.035
Zn	1/Week	Monthly	24	0.017	0.040	0.090	0.41	1.67	0.067
		Daily	101	0.005	0.039	0.110	0.57	2.99	0.12

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-1.9 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F134
Subcategory(ies): Cadmium Pigments and Salts
Other Products: None
Discharge Status: Direct (001)
Monitoring Period: January, 1979 to December, 1981
Treatment Technology: Eq, S, FL(p)

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd	1/Week	Monthly	35	0.076	0.33	0.81	0.545	1.89	0.62
		Daily	148	0.01	0.33	1.65	0.939	4.65	1.5
NH_3-N	1/Week	Monthly	35	28.4	150.6	393	0.52	1.85	279
		Daily	167	4.8	145.8	1005	1.07	5.23	763

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

COBALT SALTS

TABLE A-2.1 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F117
Subcategory(ies):	Cadmium, Cobalt and Nickel Salts
Other Products:	Numerous Catalysts
Discharge Status:	Direct
Monitoring Period:	January, 1983
Treatment Technology:	Cadmium and Cobalt Salts Wastewater Treatment: Pcp, FL(p)

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
pH	Grab Basis	Daily	1	N/A	6.81	N/A	N/A	N/A	N/A
TSS	Grab Basis	Daily	1	N/A	1.2	N/A	N/A	N/A	N/A
Cd	Grab Basis	Daily	1	N/A	0.05	N/A	N/A	N/A	N/A
Co	Grab Basis	Daily	1	N/A	0.09	N/A	N/A	N/A	N/A
Pb	Grab Basis	Daily	1	N/A	0.002	N/A	N/A	N/A	N/A

N/A - Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-2.2 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F118
Subcategory(ies): Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (002)
Monitoring Period: September 1980 to November 1982 (NPDES Quarterly Reports)
Treatment Technology: Eq, Pcp, CL, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	1/Month	Monthly	9	0.02	0.066	0.13	0.68	2.12	0.14
CN (Free)	1/Month	Monthly	9	<0.01	<0.07	<0.1	0.64	2.05	<0.14
Co	1/Month	Monthly	9	0.05	0.11	0.26	1.77	3.90	0.43
Cu	1/Month	Monthly	9	1.7	2.4	2.9	0.20	1.33	3.2
Ni	1/Month	Monthly	9	0.27	0.62	1.6	0.61	2.00	1.2
Zn	1/Month	Monthly	9	0.30	0.93	1.5	0.42	1.69	1.6
TSS	1/Month	Monthly	9	4.6	6.7	8.8	0.21	1.34	9.0

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-2.3 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F118
Subcategory(ies): Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (002)
Monitoring Period: May 1979 to June 1981 (Compliance Monitoring)
Treatment Technology: Eq, Pcp, CL, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	Irregular	Daily	3	0.17	2.2	5.3	N/A	N/A	N/A
CN (Free)	Irregular	Daily	3	0.16	2.2	5.3	N/A	N/A	N/A
Co	Irregular	Daily	3	0.04	0.077	0.14	N/A	N/A	N/A
Cr	Irregular	Daily	1	N/A	0.01	N/A	N/A	N/A	N/A
Cu	Irregular	Daily	3	1.1	5.2	11	N/A	N/A	N/A
Ni	Irregular	Daily	3	0.2	0.68	1.2	N/A	N/A	N/A
Zn	Irregular	Daily	3	0.46	0.52	0.58	N/A	N/A	N/A
TSS	Irregular	Daily	3	1.6	4.1	7.0	N/A	N/A	N/A

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-2.4 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F118
Subcategory(ies):	Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products:	Other Inorganic Chemicals
Discharge Status:	Direct (002)
Monitoring Period:	August, 1978 to May, 1980 (Supplementary Monitoring)
Treatment Technology:	Eq, Pcp, CL, pH

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	1/Month	Daily	13	<0.05	<0.13	0.19	0.94	4.65	0.60
Cd	1/Month	Daily	13	(All values reported as <0.01)					
Cr	1/Month	Daily	13	(All values reported as <0.03)					
Pb	1/Month	Daily	13	(All values reported as <0.01)					
Fluorides	1/Month	Daily	13	5	10.6	20	0.38	1.04	11.0
Fluoborates	1/Month	Daily	13	(All values reported as <0.08)					
Arsenate	1/Month	Daily	13	(All values reported as <0.01)					

Also monitor Ba, Sn, Borates, Acetates, BOD, COD, TOC

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-2.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F119
Subcategory(ies):	Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products:	Numerous Organic & Inorganic Chemicals
Discharge Status:	Indirect
Monitoring Period:	December, 1978 to June, 1980
Treatment Technology:	Neut, Floc, CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd	Daily for 1 week per quarter	Monthly	6	0.03	0.11	0.24	0.89	2.46	0.27
		Daily	30	0.02	0.11	1.08	1.82	8.05	0.89
Cu	Daily for 1 week per quarter	Monthly	6	3.11	5.16	7.1	0.28	1.46	7.5
		Daily	30	0.069	5.15	14.9	0.68	3.48	17.9
Cr	Daily for 1 week per quarter	Monthly	6	2.31	3.76	5.74	0.36	1.59	6.0
		Daily	30	0.65	3.76	11.4	0.72	3.66	13.8
Ni	Daily for 1 week per quarter	Monthly	6	0.63	1.6	3:8	0.69	2.13	3.4
		Daily	30	0.35	1.6	5.7	0.73	3.70	5.9
Zn	Daily for 1 week per quarter	Monthly	6	0.038	0.31	0.68	0.76	2.25	0.70
		Daily	30	0.02	0.31	1.26	1.12	5.44	1.69
CN(A)	Daily for 1 week per quarter	Monthly	5	<0.001	<0.001	0.001	0.00	1.00	<0.001
		Daily	19	<0.001	<0.001	0.001	0.00	1.00	<0.001

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 2.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS (Cont.)

Facility Code: F119 (Cont.)
Subcategory(ies): Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products: Numerous Organic & Inorganic Chemicals
Discharge Status: Indirect
Monitoring Period: December 1978 to June 1980
Treatment Technology: Neut, Floc, CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN(T)	Daily for 1 week per quarter	Monthly	5	0.001	0.09	0.38	1.82	3.98	0.36
		Daily	20	<0.001	0.08	1.28	3.54	11.7	0.94

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*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-2.6 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F124
Subcategory(ies): Cadmium, Cobalt and Nickel Salts
Other Products: Other Organic and Inorganic Chemicals
Discharge Status: Direct (001)
Monitoring Period: January 2, 1981 to February 28, 1983
Treatment Technology: Eq, Floc, Pcp, CL, FL(s), pH, Sd

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics (1)					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Co	1/Day	Monthly	26	0.50	0.97	1.70	0.27	1.44	1.4
		Daily	657	0.008	0.97	7.7	0.74	3.75	3.6
Ni	1/Day	Monthly	26	0.39	0.69	1.14	0.32	1.52	1.0
		Daily	657	0.012	0.69	10.4	0.98	4.83	3.3
Cd	1/Day	Monthly	26	0.032	0.063	0.17	0.47	1.78	0.11
		Daily	657	0.007	0.063	0.59	1.12	5.45	0.34

(1) Effluent concentrations reported here were flow proportioned to account for commingling with non-contact cooling water before discharge.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-2.7 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F139
Subcategory(ies): Nickel and Cobalt Salts
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (001)
Monitoring Period: January, 1981 to February, 1983
Treatment Technology: Eq, CL, Neut (2), FL(p)

Parameter(1) (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics No.	Min.	Avg.	Max.	CV	Variability Factor	Performance Standard (P)
TSS	5/Month	Monthly	25	5.1	14.5	72.3	0.90	2.48	36
TSS	5/Month	Daily	123	3.0	14.7	154	1.18	5.70	84
Co	1/day	Monthly	25	0.50	1.92	7.8	0.97	2.59	5.0
Co	1/day	Daily	745	0.08	1.91	135	3.22	11.2	21.4
Ni	1/day	Monthly	18	0.29	1.07	3.8	0.74	2.2	2.4
Ni	1/day	Daily	535	0.05	1.07	18.0	2.83	10.5	11.2

(1) Also monitor manganese

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

COPPER SALTS

TABLE A-3.1 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F115
Subcategory(ies): Copper Salts
Other Products: Organic and Inorganic Chemicals
Discharge Status: Direct (001)
Monitoring Period: January, 1981 to March, 1983
Treatment Technology: Pcp, Sd, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	2/Week	Monthly	27	6.8	17.1	29.2	0.33	1.54	26
Cd	2/Week	Monthly	3	0.04	0.05	0.08	N/A	N/A	N/A
Cu	2/Week	Monthly	27	0.28	0.43	0.63	0.26	1.43	0.61
Pb	2/Week	Monthly	3	0.24	0.27	0.30	N/A	N/A	N/A
Zn	2/Week	Monthly	3	0.06	0.07	0.09	N/A	N/A	N/A

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 3.2 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F118
Subcategory(ies): Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (002)
Monitoring Period: September 1980 to November 1982 (NPDES Quarterly Reports)
Treatment Technology: Eq, Pcp, CL, pH

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	1/Month	Monthly	9	0.02	0.066	0.13	0.68	2.12	0.14
CN (Free)	1/Month	Monthly	9	<0.01	<0.07	<0.1	0.64	2.05	<0.14
Co	1/Month	Monthly	9	0.05	0.11	0.26	1.77	3.90	0.43
Cu	1/Month	Monthly	9	1.7	2.4	2.9	0.20	1.33	3.2
Ni	1/Month	Monthly	9	0.27	0.62	1.6	0.61	2.00	1.2
Zn	1/Month	Monthly	9	0.30	0.93	1.5	0.42	1.69	1.6
TSS	1/Month	Monthly	9	4.6	6.7	8.8	0.21	1.34	9.0

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-3.3 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F118

Subcategory(ies): Cobalt, Copper and Nickel Salts and Zinc Chloride

Other Products: Other Inorganic Chemicals

Discharge Status: Direct (002)

Monitoring Period: May 1979 to June 1981 (Compliance Monitoring)

Treatment Technology: Eq, Pcp, CL, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	Irregular	Daily	3	0.17	2.2	5.3	N/A	N/A	N/A
CN (Free)	Irregular	Daily	3	0.16	2.2	5.3	N/A	N/A	N/A
Co	Irregular	Daily	3	0.04	0.077	0.14	N/A	N/A	N/A
Cr	Irregular	Daily	1	N/A	0.01	N/A	N/A	N/A	N/A
Cu	Irregular	Daily	3	1.1	5.2	11	N/A	N/A	N/A
Ni	Irregular	Daily	3	0.2	0.68	1.2	N/A	N/A	N/A
Zn	Irregular	Daily	3	0.46	0.52	0.58	N/A	N/A	N/A
TSS	Irregular	Daily	3	1.6	4.1	7.0	N/A	N/A	N/A

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 3.4 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F118
Subcategory(ies):	Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products:	Other Inorganic Chemicals
Discharge Status:	Direct (002)
Monitoring Period:	August, 1978 to May, 1980 (Supplementary Monitoring)
Treatment Technology:	Eq, Pcp, CL, pH

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	1/Month	Daily	13	<0.05	<0.13	0.19	0.94	4.65	0.60
Cd	1/Month	Daily	13	(All values reported as <0.01)					
Cr	1/Month	Daily	13	(All values reported as <0.03)					
Pb	1/Month	Daily	13	(All values reported as <0.01)					
Fluorides	1/Month	Daily	13	5	10.6	20	0.38	1.04	11.0
Fluoborates	1/Month	Daily	13	(All values reported as <0.08)					
Arsenate	1/Month	Daily	13	(All values reported as <0.01)					

Also monitor Ba, Sn, Borates, Acetates, BOD, COD, TOC

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-3.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F119
Subcategory(ies): Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products: Numerous Organic & Inorganic Chemicals
Discharge Status: Indirect
Monitoring Period: December, 1978 to June, 1980
Treatment Technology: Neut, Floc, CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd	Daily for 1 week per quarter	Monthly	6	0.03	0.11	0.24	0.89	2.46	0.27
		Daily	30	0.02	0.11	1.08	1.82	8.05	0.89
Cu	Daily for 1 week per quarter	Monthly	6	3.11	5.16	7.1	0.28	1.46	7.5
		Daily	30	0.069	5.15	14.9	0.68	3.48	17.9
Cr	Daily for 1 week per quarter	Monthly	6	2.31	3.76	5.74	0.36	1.59	6.0
		Daily	30	0.65	3.76	11.4	0.72	3.66	13.8
Ni	Daily for 1 week per quarter	Monthly	6	0.63	1.6	3.8	0.69	2.13	3.4
		Daily	30	0.35	1.6	5.7	0.73	3.70	5.9
Zn	Daily for 1 week per quarter	Monthly	6	0.038	0.31	0.68	0.76	2.25	0.70
		Daily	30	0.02	0.31	1.26	1.12	5.44	1.69
CN(A)	Daily for 1 week per quarter	Monthly	5	<0.001	<0.001	0.001	0.00	1.00	<0.001
		Daily	19	<0.001	<0.001	0.001	0.00	1.00	<0.001

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-3.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS (Cont.)

Facility Code:	F119 (Cont.)
Subcategory(ies):	Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products:	Numerous Organic & Inorganic Chemicals
Discharge Status:	Indirect
Monitoring Period:	December 1978 to June 1980
Treatment Technology:	Neut, Floc, CL

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN(T)	Daily for 1 week per quarter	Monthly	5	0.001	0.09	0.38	1.82	3.98	0.36
		Daily	20	<0.001	0.08	1.28	3.54	11.7	0.94

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 3.6 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F127
Subcategory(ies): Copper Salts
Other Products: Other Organic and Inorganic Chemicals
Discharge Status: Direct (002)
Monitoring Period: January 1981 to February 1983
Treatment Technology: Pcp, AR, CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cu	2/week	Monthly	25	0.02	0.12	1.1	1.84	4.02	0.48

basis of Daily Maximum values reported on NPDES Monthly reports.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 3.7 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F133
Subcategory(ies): Copper Salts
Other Products: Numerous Catalysts and Pigments
Discharge Status: Indirect
Monitoring Period: January, 1979 to June, 1980
Treatment Technology: Main Wastewater Treatment Plant: Eq, Neut, FL(s) (Final Treatment of Several Independent Treatment Systems, Including Copper Treatment

Parameter[(1)] (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics No.	Min.	Avg.	Max.	CV	Variability Factor	Performance Standard (P)
TSS	1/Week (8 hr. comp.)	Monthly	18	153	334	520	0.36	1.59	531
		Daily	77	41	322	820	0.56	2.94	947
TSS	4/Month (7 day comp.)	Monthly	18	264	361	505	0.24	1.39	502
As	1/Month	Monthly	17	<0.1	<0.1	<0.1	0	1.0	<0.1[(2)]
		Daily	18	<0.1	<0.1	<0.1	0	1.0	<0.1[(2)]
Cd	1/Week	Monthly	18	<0.01	0.03	0.07	0.55	1.90	0.06
		Daily	75	<0.01	0.03	0.18	0.90	4.47	0.13
Co	1/Month	Monthly	17	<0.1	0.12	0.2	0.33	1.54	0.18
		Daily	20	<0.1	0.13	0.3	0.44	2.44	0.32

(1) Also monitors TDS, Al (total and dissolved), Ba, Mo, Zr, Fluoride, PO_4-P, COD and Oil & Greas

(2) All arsenic samples reported as <0.1

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-3.7 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS (Cont.)

Facility Code:	F133 (Cont.)
Subcategory(ies):	Copper Salts
Other Products:	Numerous Catalysts and Pigments
Discharge Status:	Indirect
Monitoring Period:	January, 1979 to June, 1980
Treatment Technology:	Main Wastewater Treatment Plant: Eq, Neut, FL(s) (Final Treatment of Several Independent Treatment Systems, Including Copper Treatment)

Parameter[(1)] (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cr	1/Month	Monthly	17	<0.1	0.11	0.2	0.22	1.36	0.15
		Daily	19	<0.1	0.11	0.2	0.22	1.62	0.18
Cu	1/Week	Monthly	18	0.5	1.3	3.0	0.56	1.92	2.5
		Daily	78	0.1	1.3	9.4	1.07	5.23	6.8
Hg	1/Month	Monthly	16	<0.001	0.002	0.004	0.5	1.8	0.004
		Daily	17	<0.001	0.002	0.004	0.58	3.03	0.006
Ni	1/Week	Monthly	18	0.4	2.6	17	1.53	3.51	9.1
		Daily	77	0.1	2.5	61.9	3.05	10.9	27.
Pb	1/Month	Monthly	18	<0.1	0.14	0.28	0.29	1.48	0.21
		Daily	77	<0.1	0.13	0.4	0.51	2.73	0.35
Zn	1/Week	Monthly	17	<0.1	0.14	0.4	0.62	2.02	0.28
		Daily	20	<0.1	0.15	0.7	0.93	4.61	0.69
NH_3-N	1/Week	Monthly	18	69	207	758	0.76	2.25	466
		Daily	76	<1	189	850	0.78	3.93	743

(1) Also monitor TDS, Al (total and dissolved), Ba, Mo, Zr, Fluoride, PO_4-P, COD and Oil and Grease.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-3.8 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F133
Subcategory(ies):	Copper Salts
Other Products:	Numerous Catalysts
Discharge Status:	Indirect
Monitoring Period:	October 1980 to November, 1980
Treatment Technology:	Main Wastewater Treatment Plant: Eq, Neut, FL(s) (Final Treatment of Several Independent Treatment Systems, Including Copper Treatment)

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Ag	Irregular	Daily	3	0.00	0.007	0.01	0.9	4.47	0.031
As	Irregular	Daily	3	0.00	<0.03	<0.1	1.7	7.66	0.23
Ba	Irregular	Daily	3	0.3	0.57	1.0	0.67	3.43	2.0
Cd	Irregular	Daily	3	0.03	0.073	0.13	0.70	3.57	0.26
Cr	Irregular	Daily	3	0.1	0.2	0.3	0.5	2.69	0.54
Cu	Irregular	Daily	3	6.9	8.1	8.8	0.13	1.34	11
Hg	Irregular	Daily	3	<0.001	<0.001	0.001	0.0	1.00	0.001
Ni	Irregular	Daily	3	1.7	5.3	12.6	1.2	5.78	31
Pb	Irregular	Daily	3	0.10	0.13	0.2	0.4	2.28	0.30
Se	Irregular	Daily	3	0.00	0.02	0.04	1.0	4.92	0.10

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 3.9 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F133
Subcategory(ies): Copper Salts
Other Products: Numerous Catalysts
Discharge Status: Indirect
Monitoring Period: October 1980 to November, 1980
Treatment Technology: Copper Wastewater Treatment: Pcp, S, FL(p)

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Ag	Irregular	Daily	3	0.02	0.04	0.05	0.43	2.40	0.10
As	Irregular	Daily	3	0.00	<0.03	<0.1	1.7	7.66	0.23
Ba	Irregular	Daily	3	1.0	5.5	12.7	1.15	5.57	30.6
Cd	Irregular	Daily	3	0.03	0.10	0.18	0.76	3.84	0.38
Cr	Irregular	Daily	3	0.1	0.33	0.6	0.76	3.84	1.27
Cu	Irregular	Daily	3	1.0	1.8	3.3	0.70	3.57	6.43
Hg	Irregular	Daily	3	<0.001	<0.001	0.001	0.0	1.00	0.001
Ni	Irregular	Daily	3	0.2	0.37	0.6	0.57	2.99	1.11
Pb	Irregular	Daily	3	0.2	0.37	0.5	0.42	2.36	0.87
Se	Irregular	Daily	3	0.1	0.25	0.5	0.89	4.43	1.11

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

NICKEL SALTS

TABLE A-4.1 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F117
Subcategory(ies): Cadmium, Cobalt and Nickel Salts
Other Products: Numerous Catalysts
Discharge Status: Direct
Monitoring Period: January, 1983
Treatment Technology: Nickel Treatment System: Pcp, FL(s), pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics No.	Min.	Avg.	Max.	CV	Variability Factor	Performance Standard (P)
pH	Grab Basis	Daily	3	N/A	8.65	N/A	N/A	N/A	N/A
TSS	Grab Basis	Daily	3	N/A	1.4	N/A	N/A	N/A	N/A
Ni	Grab Basis	Daily	3	N/A	0.7	N/A	N/A	N/A	N/A

N/A - Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.2 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F117
Subcategory(ies):	Cadmium, Cobalt and Nickel Salts
Other Products:	Numerous Catalysts
Discharge Status:	Direct
Monitoring Period:	January, 1983
Treatment Technology:	Fluoride Treatment System: Neut (Lime), Floc & CL, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
pH	Grab Basis	Daily	1	N/A	6.80	N/A	N/A	N/A	N/A
TSS	Grab Basis	Daily	1	N/A	5.0	N/A	N/A	N/A	N/A
Ni	Grab Basis	Daily	1	N/A	0.09	N/A	N/A	N/A	N/A
Flucride	Grab Basis	Daily	1	N/A	13	N/A	N/A	N/A	N/A

N/A - Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.3 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F118
Subcategory(ies): Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (002)
Monitoring Period: September 1980 to November 1982 (NPDES Quarterly Reports)
Treatment Technology: Eq, Pcp, CL, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics No.	Min.	Avg.	Max.	CV	Variability Factor	Performance Standard (P)
CN (Total)	1/Month	Monthly	9	0.02	0.066	0.13	0.68	2.12	0.14
CN (Free)	1/Month	Monthly	9	<0.01	<0.07	<0.1	0.64	2.05	<0.14
Co	1/Month	Monthly	9	0.05	0.11	0.26	1.77	3.90	0.43
Cu	1/Month	Monthly	9	1.7	2.4	2.9	0.20	1.33	3.2
Ni	1/Month	Monthly	9	0.27	0.62	1.6	0.61	2.00	1.2
Zn	1/Month	Monthly	9	0.30	0.93	1.5	0.42	1.69	1.6
TSS	1/Month	Monthly	9	4.6	6.7	8.8	0.21	1.34	9.0

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.4 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F118

Subcategory(ies): Cobalt, Copper and Nickel Salts and Zinc Chloride

Other Products: Other Inorganic Chemicals

Discharge Status: Direct (002)

Monitoring Period: May 1979 to June 1981 (Compliance Monitoring)

Treatment Technology: Eq, Pcp, CL, pH

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	Irregular	Daily	3	0.17	2.2	5.3	N/A	N/A	N/A
CN (Free)	Irregular	Daily	3	0.16	2.2	5.3	N/A	N/A	N/A
Co	Irregular	Daily	3	0.04	0.077	0.14	N/A	N/A	N/A
Cr	Irregular	Daily	1	N/A	0.01	N/A	N/A	N/A	N/A
Cu	Irregular	Daily	3	1.1	5.2	11	N/A	N/A	N/A
Ni	Irregular	Daily	3	0.2	0.68	1.2	N/A	N/A	N/A
Zn	Irregular	Daily	3	0.46	0.52	0.58	N/A	N/A	N/A
TSS	Irregular	Daily	3	1.6	4.1	7.0	N/A	N/A	N/A

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F118
Subcategory(ies):	Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products:	Other Inorganic Chemicals
Discharge Status:	Direct (002)
Monitoring Period:	August, 1978 to May, 1980 (Supplementary Monitoring)
Treatment Technology:	Eq, Pcp, CL, pH

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	1/Month	Daily	13	<0.05	<0.13	0.19	0.94	4.65	0.60
Cd	1/Month	Daily	13	(All values reported as <0.01)					
Cr	1/Month	Daily	13	(All values reported as <0.03)					
Pb	1/Month	Daily	13	(All values reported as <0.01)					
Fluorides	1/Month	Daily	13	5	10.6	20	0.38	1.04	11.0
Fluoborates	1/Month	Daily	13	(All values reported as <0.08)					
Arsenate	1/Month	Daily	13	(All values reported as <0.01)					

Also monitor Ba, Sn, Borates, Acetates, BOD, COD, TOC

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.6 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F119
Subcategory(ies): Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products: Numerous Organic & Inorganic Chemicals
Discharge Status: Indirect
Monitoring Period: December, 1978 to June, 1980
Treatment Technology: Neut, Floc, CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cd	Daily for 1 week per quarter	Monthly	6	0.03	0.11	0.24	0.89	2.46	0.27
		Daily	30	0.02	0.11	1.08	1.82	8.05	0.89
Cu	Daily for 1 week per quarter	Monthly	6	3.11	5.16	7.1	0.28	1.46	7.5
		Daily	30	0.069	5.15	14.9	0.68	3.48	17.9
Cr	Daily for 1 week per quarter	Monthly	6	2.31	3.76	5.74	0.36	1.59	6.0
		Daily	30	0.65	3.76	11.4	0.72	3.66	13.8
Ni	Daily for 1 week per quarter	Monthly	6	0.63	1.6	3.8	0.69	2.13	3.4
		Daily	30	0.35	1.6	5.7	0.73	3.70	5.9
Zn	Daily for 1 week per quarter	Monthly	6	0.038	0.31	0.68	0.76	2.25	0.70
		Daily	30	0.02	0.31	1.26	1.12	5.44	1.69
CN(A)	Daily for 1 week per quarter	Monthly	5	<0.001	<0.001	0.001	0.00	1.00	<0.001
		Daily	19	<0.001	<0.001	0.001	0.00	1.00	<0.001

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.6 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS (Cont.)

Facility Code:	F119 (Cont.)
Subcategory(ies):	Cadmium Pigments, Cadmium, Cobalt, Copper and Nickel Salts
Other Products:	Numerous Organic & Inorganic Chemicals
Discharge Status:	Indirect
Monitoring Period:	December 1978 to June 1980
Treatment Technology:	Neut, Floc, CL

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN(T)	Daily for 1 week per quarter	Monthly	5	0.001	0.09	0.38	1.82	3.98	0.36
		Daily	20	<0.001	0.08	1.28	3.54	11.7	0.94

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.7 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F124
Subcategory(ies): Cadmium, Cobalt and Nickel Salts
Other Products: Other Organic and Inorganic Chemicals
Discharge Status: Direct (001)
Monitoring Period: January 2, 1981 to February 28, 1983
Treatment Technology: Eq, Floc, Pcp, CL, FL(s), pH, Sd

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics (1)					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Co	1/Day	Monthly	26	0.50	0.97	1.70	0.27	1.44	1.4
		Daily	657	0.008	0.97	7.7	0.74	3.75	3.6
Ni	1/Day	Monthly	26	0.39	0.69	1.14	0.32	1.52	1.0
		Daily	657	0.012	0.69	10.4	0.98	4.83	3.3
Cd	1/Day	Monthly	26	0.032	0.063	0.17	0.47	1.78	0.11
		Daily	657	0.007	0.063	0.59	1.12	5.45	0.34

(1) Effluent concentrations reported here were flow proportioned to account for commingling with non-contact cooling water before discharge.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 4.8 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F125
Subcategory(ies): Cadmium and Nickel Salts and Zinc Chloride
Other Products: Inorganic Chemicals
Discharge Status: Direct
Monitoring Period: January, 1981 to January, 1983
Treatment Technology: Pcp, CL, Sd

Parameter[1] (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics No.	Min.	Avg.	Max.	CV	Variability Factor	Performance Standard (P)
TSS	1/week	Monthly	24	4	8.7	18.2	0.41	1.67	14.5
Cd	1/week	Monthly	24	All values reported as "Not Detected"					
Co	1/week	Monthly	25	All values reported as "Not Detected"					
Cu (2)	1/week	Monthly	11	0.055	0.093	0.14	0.25	1.41	0.13
	1/week	Daily	11	0.11	0.14	0.18	0.17	1.30	0.18
Ni	1/week	Monthly	24	All values reported as "Not Detected", except 7/82 when the Avg. = 0.04 mg/1 and the Max = 0.10 mg/1					
Pb	1/week	Monthly	24	All values reported as "Not Detected"					
Zn	1/week	Monthly	24	0.010	0.15	0.32	0.51	1.84	0.28

(1) Mn is also monitored. However Mn was reported as "Not Detected" throughout the period.

(2) Copper was detected in the wastewater effluent only one month during the period prior to 3/82. At this time a change occurred in the process, resulting in copper detection every month. Therefore the period considered in this analysis was 3/82 to 1/83.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-4.9 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F139
Subcategory(ies):	Nickel and Cobalt Salts
Other Products:	Other Inorganic Chemicals
Discharge Status:	Direct (001)
Monitoring Period:	January, 1981 to February, 1983
Treatment Technology:	Eq, CL, Neut (2), FL(p)

Parameter[(1)] (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	5/Month	Monthly	25	5.1	14.5	72.3	0.90	2.48	36
TSS	5/Month	Daily	123	3.0	14.7	154	1.18	5.70	84
Co	1/day	Monthly	25	0.50	1.92	7.8	0.97	2.59	5.0
Co	1/day	Daily	745	0.08	1.91	135	3.22	11.2	21.4
Ni	1/day	Monthly	18	0.29	1.07	3.8	0.74	2.2	2.4
Ni	1/day	Daily	535	0.05	1.07	18.0	2.83	10.5	11.2

(1) Also monitor manganese

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

SODIUM CHLORATE

TABLE A- 5.1 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F103
Subcategory(ies): Sodium Chlorate
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (001)
Monitoring Period: February, 1980
Treatment Technology: None

Parameter (mg/1)	(1) Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
As	Irregular	N/A	2	<0.005	<0.005	<0.005	N/A	N/A	N/A
Be	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Cd	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Cr	Irregular	N/A	2	<0.001	0.011	0.021	N/A	N/A	N/A
Cu	Irregular	N/A	2	<0.004	<0.004	<0.004	N/A	N/A	N/A
Hg	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Ni	Irregular	N/A	2	0.003	0.004	0.004	N/A	N/A	N/A
Pb	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Sb	Irregular	N/A	2	<0.005	<0.005	<0.005	N/A	N/A	N/A
Se	Irregular	N/A	2	<0.005	<0.005	<0.005	N/A	N/A	N/A
Tl	Irregular	N/A	2	<0.002	<0.002	<0.002	N/A	N/A	N/A
Zn	Irregular	N/A	2	<0.010	0.018	0.025	N/A	N/A	N/A

(1) Also sampled for priority organic pollutants

N/A = Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 5.2 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F103
Subcategory(ies):	Sodium Chlorate
Other Products:	Other Inorganic Chemicals
Discharge Status:	Direct (002)
Monitoring Period:	February, 1980
Treatment Technology:	None

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
As	Irregular	N/A	2	<0.005	<0.005	<0.005	N/A	N/A	N/A
Be	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Cd	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Cr	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Cu	Irregular	N/A	2	0.008	0.009	0.010	N/A	N/A	N/A
Hg	Irregular	N/A	2	<0.001	<0.001	<0.001	N/A	N/A	N/A
Ni	Irregular	N/A	2	0.009	0.010	0.010	N/A	N/A	N/A
Pb	Irregular	N/A	2	<0.001	0.002	0.002	N/A	N/A	N/A
Sb	Irregular	N/A	2	<0.005	<0.005	<0.005	N/A	N/A	N/A
Se	Irregular	N/A	2	<0.005	<0.005	<0.005	N/A	N/A	N/A
Tl	Irregular	N/A	2	<0.002	<0.002	<0.002	N/A	N/A	N/A
Zn	Irregular	N/A	2	0.012	0.012	0.012	N/A	N/A	N/A

N/A = Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 5.3 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F103
Subcategory(ies): Sodium Chlorate
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (001 West)
Monitoring Period: January, 1979 to June, 1980
Treatment Technology: None

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cr (VI)	1/Month		19	(All values reported as <0.04 or <0.06)					
Cl^-	1/Month(1)		10	(All values reported as 0)					
Cl^-	1/Day(2)	Monthly	12	11.2	17.0	21.8	0.21	1.34	23
		Daily	330	6	17.6	70	0.46	2.52	44
ClO_3^-	1/Day(3)	Monthly	6	34.1	58.1	133	0.64	2.05	119
		Daily	31	7	40.9	145	0.74	3.75	153

(1) Reported from 10/79 to 6/80
(2) Reported on 7/3, 11, 12, 13, 17, 20 and 8/1/79 and daily from 8/8/79 to 6/30/80
(3) Reported on 7/3, 11, 12, 13, 17, 20 and 8/8/79; 5/12 and 5/21/80 and daily from 6/10 to 6/30/80

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-5.4 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F103
Subcategory(ies): Sodium Chlorate
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (002 North)
Monitoring Period: January, 1979 to June, 1980
Treatment Technology: None

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics No.	Min.	Avg.	Max.	CV	Variability Factor	Performance Standard (P)
Cr (VI)	1/Month		19	(All values reported as <0.04 or <0.06)					
Cl^-	1/Month(1)		9	(All values reported as 0)					
Cl^-	1/Day(2)	Monthly	11	13.0	21.5	29.1	0.23	1.38	30
		Daily	324	1	21.5	100	0.57	1.93	41
ClO_3^-	1/Day(3)	Monthly	3	4	4.7	6.2	0.27	1.44	7
		Daily	21	3	6.0	18	0.58	1.95	12

(1) Reported from 10/79 to 6/80
(2) Reported from 8/9/79 to 6/30/80
(3) Reported from 5/9/79, 5/12/80, and daily from 6/10/80 to 6/30/80

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 5.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F147
Subcategory(ies):	Sodium Chlorate
Other Products:	Titanium Dioxide, Specialty Manganese Metals
Discharge Status:	Direct (201)
Monitoring Period:	January 1979 to June 1980
Treatment Technology:	Neut (2), Sd

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	1/week	Monthly	18	2.2	5.34	17.4	0.64	2.05	11
Cr (Tot.)	1/week	Monthly	18	0.018	0.079	0.26	0.83	2.36	0.19
Fe	2/Month	Monthly	18	0.05	0.18	0.55	0.78	2.28	0.41
Mn	1/week	Monthly	18	0.05	1.24	7.6	1.63	3.67	4.6
NH_3-N	1/week	Monthly	18	0.58	1.56	3.78	0.61	2.00	3.1

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 5.6 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F147
Subcategory(ies): Sodium Chlorate
Other Products: Titanium Dioxide, Specialty Manganese Metals
Discharge Status: Direct (201)
Monitoring Period: January, 1980 to December, 1982
Treatment Technology: Neut (2), Sd

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
Cr(Total)	1/Week	Monthly	30	0.02	0.11	0.59	0.99	2.62	0.29

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 5.7 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F149
Subcategory(ies):	Sodium Chlorate
Other Products:	Chlor-alkali, Organic Chemicals
Discharge Status:	Direct (102)
Monitoring Period:	July, 1979 to June, 1980
Treatment Technology:	Wastewater streams from $NaClO_3$, chlor-alkali, raw water treatment and boiler blowdown are combined and neutralized.

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	2-4/week	Monthly(1)	6	459	732.5	1,153	0.42	1.69	1238
		Daily(2)	72	121	734	5,495	1.195	5.76	4228

(1) Reported from 1/80 to 6/80
(2) Reported from 1/80 to 7/80 and two earlier samples on 7/9/79 and 12/28/79

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

ZINC CHLORIDE

TABLE A-6.1 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F118
Subcategory(ies):	Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products:	Other Inorganic Chemicals
Discharge Status:	Direct (002)
Monitoring Period:	September 1980 to November 1982 (NPDES Quarterly Reports)
Treatment Technology:	Eq, Pcp, CL, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	1/Month	Monthly	9	0.02	0.066	0.13	0.68	2.12	0.14
CN (Free)	1/Month	Monthly	9	<0.01	<0.07	<0.1	0.64	2.05	<0.14
Co	1/Month	Monthly	9	0.05	0.11	0.26	1.77	3.90	0.43
Cu	1/Month	Monthly	9	1.7	2.4	2.9	0.20	1.33	3.2
Ni	1/Month	Monthly	9	0.27	0.62	1.6	0.61	2.00	1.2
Zn	1/Month	Monthly	9	0.30	0.93	1.5	0.42	1.69	1.6
TSS	1/Month	Monthly	9	4.6	6.7	8.8	0.21	1.34	9.0

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-6.2 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F118
Subcategory(ies):	Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products:	Other Inorganic Chemicals
Discharge Status:	Direct (002)
Monitoring Period:	May 1979 to June 1981 (Compliance Monitoring)
Treatment Technology:	Eq, Pcp, CL, pH

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	Irregular	Daily	3	0.17	2.2	5.3	N/A	N/A	N/A
CN (Free)	Irregular	Daily	3	0.16	2.2	5.3	N/A	N/A	N/A
Co	Irregular	Daily	3	0.04	0.077	0.14	N/A	N/A	N/A
Cr	Irregular	Daily	1	N/A	0.01	N/A	N/A	N/A	N/A
Cu	Irregular	Daily	3	1.1	5.2	11	N/A	N/A	N/A
Ni	Irregular	Daily	3	0.2	0.68	1.2	N/A	N/A	N/A
Zn	Irregular	Daily	3	0.46	0.52	0.58	N/A	N/A	N/A
TSS	Irregular	Daily	3	1.6	4.1	7.0	N/A	N/A	N/A

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-6.3 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F118
Subcategory(ies): Cobalt, Copper and Nickel Salts and Zinc Chloride
Other Products: Other Inorganic Chemicals
Discharge Status: Direct (002)
Monitoring Period: August, 1978 to May, 1980 (Supplementary Monitoring)
Treatment Technology: Eq, Pcp, CL, pH

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
CN (Total)	1/Month	Daily	13	<0.05	<0.13	0.19	0.94	4.65	0.60
Cd	1/Month	Daily	13	(All values reported as <0.01)					
Cr	1/Month	Daily	13	(All values reported as <0.03)					
Pb	1/Month	Daily	13	(All values reported as <0.01)					
Fluorides	1/Month	Daily	13	5	10.6	20	0.38	1.04	11.0
Fluoborates	1/Month	Daily	13	(All values reported as <0.08)					
Arsenate	1/Month	Daily	13	(All values reported as <0.01)					

Also monitor Ba, Sn, Borates, Acetates, BOD, COD, TOC

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A- 6.4 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F125
Subcategory(ies): Cadmium and Nickel Salts and Zinc Chloride
Other Products: Inorganic Chemicals
Discharge Status: Direct
Monitoring Period: January, 1981 to January, 1983
Treatment Technology: Pcp, CL, Sd

Parameter(1) (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	1/week	Monthly	24	4	8.7	18.2	0.41	1.67	14.5
Cd	1/week	Monthly	24	All values reported as "Not Detected"					
Co	1/week	Monthly	25	All values reported as "Not Detected"					
Cu(2)	1/week	Monthly	11	0.055	0.093	0.14	0.25	1.41	0.13
Ni	1/week	Monthly	24	All values reported as "Not Detected", except 7/82 when the Avg. = 0.04 mg/l and the Max = 0.10 mg/l					
Pb	1/week	Monthly	24	All values reported as "Not Detected"					
Zn	1/week	Monthly	24	0.010	0.15	0.32	0.51	1.84	0.28

(1) Mn is also monitored. However Mn was reported as "Not Detected" throughout the period.

(2) Copper was detected in the wastewater effluent only one month during the period prior to 3/82. At this time a change occurred in the process, resulting in copper detection every month. Therefore the period considered in this analysis was 3/82 to 1/83.

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-6.5 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code: F140
Subcategory(ies): Zinc Chloride
Other Products: Inorganic Chemicals
Discharge Status: Direct (001)
Monitoring Period: November 1979 to June 1982
Treatment Technology: Neut, Sd

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	2/week	Monthly	32	8.1	13.3	20.5	0.66	2.08	28
Cd	1/week	Monthly	32	0.0074	0.012	0.024	0.28	1.46	0.018
Pb	1/week	Monthly	32	0.066	0.16	0.35	0.42	1.69	0.27
Zn	2/week	Monthly	32	0.90	1.87	3.58	0.37	1.61	3.0

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

TABLE A-6.6 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F144
Subcategory(ies):	Zinc Chloride
Other Products:	Inorganic and Organic Chemicals
Discharge Status:	Direct (004)
Monitoring Period:	January, 1978 to November, 1982
Treatment Technology:	Eq, Neut(2), CL

Parameter (mg/1)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	2/Week	Monthly	51	2	6.0	11.6	0.42	1.68	10
		Daily	440**	1	6.0	62	0.87	4.34	26
NH_3-N	2/Week	Monthly	51	2.9	7.1	11.8	0.26	1.43	10
		Daily	441	2.0	7.1	30	0.48	2.60	18
Cd	2/Week	Monthly	51	0.005	0.0086	0.042	0.64	2.05	0.018
		Daily	441	0.001	0.0087	0.073	0.83	4.16	0.036
Cr	2/Week	Monthly	51	0.011	0.0385	0.147	0.67	2.10	0.081
		Daily	441	0.001	0.0391	1.23	1.84	8.12	0.32
Pb	2/Week	Monthly	38	0.025	0.0362	0.047	0.15	1.25	0.045
		Daily	344	0.007	0.038	0.67	0.97	4.79	0.18
Zn (diss.)	2/Week	Monthly	51	0.035	0.225	0.801	0.60	1.98	0.45
		Daily	442	0.014	0.224	4.4	1.26	6.03	1.35

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

**One data point for TSS removed (284 mg/1) due to system upset.

TABLE A- 6.7 HISTORICAL EFFLUENT MONITORING DATA SUMMARY WITH VARIABILITY FACTORS AND PERFORMANCE STANDARDS

Facility Code:	F144
Subcategory(ies):	Zinc Chloride
Other Products:	Inorganic and Organic Chemicals
Discharge Status:	Direct (004)
Monitoring Period:	April, 1978 (EPA Plant Visit - Industry and EPA Analytical Results)
Treatment Technology:	Eq, Neut (2), CL

Parameter (mg/l)	Sampling Frequency	Daily or Monthly*	Historical Summary Statistics					Variability Factor	Performance Standard (P)
			No.	Min.	Avg.	Max.	CV		
TSS	Irregular	N/A	2	3	4	5	N/A	N/A	N/A
As	Irregular	N/A	2	<0.003	0.007	0.010	N/A	N/A	N/A
Cd	Irregular	N/A	2	<0.002	0.006	0.010	N/A	N/A	N/A
Cr	Irregular	N/A	2	0.036	0.041	0.045	N/A	N/A	N/A
Cu	Irregular	N/A	2	0.033	0.036	0.038	N/A	N/A	N/A
Pb	Irregular	N/A	2	<0.020	0.025	0.030	N/A	N/A	N/A
Ni	Irregular	N/A	2	<0.005	0.018	0.030	N/A	N/A	N/A
Se	Irregular	N/A	2	<0.003	0.004	0.005	N/A	N/A	N/A
Zn	Irregular	N/A	2	0.82	0.87	0.92	N/A	N/A	N/A

N/A = Not Applicable

*99% of the daily measurements expected to be less than the performance standard (P)
95% of the monthly averages expected to be less than the performance standard (P)

Appendix B

Plant F102 and F128 Wastewater Data

Table B-1. Plant F102 Effluent Data (7/21/82-11/21/83)
(Sheet 1 of 6)

DATE	CD(MG/L)	CR(MG/L)	SE(MG/L)	TSS(MG/L)	SCREEN CODE
72182	.1	.6	.04	12	0
72282	.03	.9	.06	8	0
72382	.03	1.9	.06	3	0
72682	.02	3.6	.04	1	1
72782	.02	2.1	.06	72	0
72882	.04	3.1	.06	61	1
72982	.1	4.9	.02	64	1
73082	.08	6.9	.01	39	1
80282	.08	3	.01	24	1
80382	.16	2.3	-1	84	0
80482	.04	3.6	-1	40	1
80582	.08	1.9	-1	26	0
80682	.21	.3	-1	56	0
80982	.11	.2	-1	80	0
81082	.07	1.5	-1	0	0
81182	.13	.8	.01	38	0
81282	.1	.2	.01	26	0
81382	.06	1.2	.02	80	0
81682	.1	.9	.01	24	0
81782	.09	26.6	.03	44	1
81882	.16	19	.01	46	1
81982	.07	2.1	.01	66	0
82082	.14	1.5	.02	54	0
82382	.08	.9	.01	32	0
82482	.14	.8	.01	88	2
82582	.12	.7	.01	72	0
82682	.16	.3	.01	120	2
82782	.05	.4	.03	36	0
83082	.13	.4	.03	98	2
83182	.05	.6	.15	50	0
90182	.22	.6	.02	58	0
90282	1.24	.4	.01	40	0
90382	.57	.1	.02	68	0
90782	.24	.7	.01	52	0
90882	.19	2.8	.01	84	0
90982	.18	1.9	.01	108	2
91082	.2	1.5	.01	182	2
91382	.3	1.5	.01	26	0
91482	.18	2.5	.39	68	0
91582	.07	1.1	.37	30	0
91682	.22	4.2	.64	172	2
91782	.82	2.2	.23	90	2
92082	.26	2.2	.2	50	0
92182	.13	1.3	.23	88	2
92282	.16	3.8	.14	32	1
92382	.18	1.8	.17	112	2
92482	.17	1.7	.28	24	0
92782	.1	2.9	.04	0	0
92882	.14	3	.05	28	1
92982	.22	4.5	.05	24	1

Screen Code: 0=Included in analysis; 1=Excluded since Cr>2.9mg/1
2=Excluded since TSS > 87mg/1

Entry of -1 = Data Not Available

Table B-1. Plant F10? Effluent Data (7/21/82-11/21/83)
(Sheet 2 of 6)

DATE	CD(MG/L)	CR(MG/L)	SE(MG/L)	TSS(MG/L)	SCREEN COD
93082	.14	2.6	.05	56	0
100182	.1	1.1	.03	82	0
100482	.26	1.2	.05	256	2
100582	.27	1.3	.04	212	2
100682	.25	.2	.02	66	0
100782	.49	.4	.01	368	2
100882	.33	.2	.01	58	0
101182	.38	.1	.02	18	0
101282	.68	.1	.01	62	0
101382	.39	3	.01	46	1
101482	.38	3.8	.01	112	2
101582	.46	11.05	.01	52	1
101882	.72	.52	.02	12	0
101982	.34	.3	.01	100	2
102082	.74	.09	.01	42	0
102182	1.05	.14	.01	52	0
102282	.85	.14	.08	26	0
102582	.44	.5	.09	50	0
102682	.14	3.33	.05	36	1
102782	.19	3.14	.03	30	1
102882	.15	2.5	.04	40	0
102982	.09	1.74	.1	34	0
110182	.21	1.45	.14	34	0
110282	.19	17	.07	160	2
110482	.49	16.75	.41	152	2
110582	.24	58	.73	22	1
110982	.33	1.75	.39	100	2
111082	.29	1.47	.15	98	2
111182	.22	.59	.09	82	0
111282	.24	.21	.01	102	2
111582	.43	.28	.05	192	2
111682	.15	.53	.05	176	2
111782	.32	.38	.03	114	2
111882	.4	1.8	.03	184	2
111982	.36	.72	.02	228	2
112282	.22	.49	.09	132	2
112382	.14	.73	.06	30	0
112482	.08	1.8	.03	90	2
112982	.14	1.16	.02	186	2
113082	.11	.97	.01	102	2
120182	.08	1.75	.01	70	0
120282	.1	76	.01	42	1
120382	.13	11	.01	118	2
120682	.07	2.75	.01	10	0
120782	.08	1.24	.01	78	0
120882	.11	1.27	.01	164	2
120982	.06	2.28	.01	74	0
121082	.08	2.1	.01	146	2
121382	.1	1.96	.01	72	0
121482	.57	.9	.01	88	2

Screen Code: 0=Included in analysis; 1=Excluded since Cr>2.9mg/l
2=Excluded since TSS > 87mg/l

Entry of -1 = Data Not Available

Table B-1. Plant F102 Effluent Data (7/21/82-11/21/83)
(Sheet 3 of 6)

DATE	CD(MG/L)	CR(MG/L)	SE(MG/L)	TSS(MG/L)	SCREEN CODE
121582	.19	1.92	.01	48	0
121682	.22	4.5	.01	38	1
121782	.05	4.75	.01	44	1
122082	.1	2	.01	72	0
122182	.08	3	.01	22	1
122282	.27	4.82	.01	30	1
122382	.18	4.9	.01	30	1
122682	.55	7.95	.01	14	1
122982	.82	3.98	.01	504	2
10383	.11	2.52	.01	0	0
10483	.24	3.92	.01	0	1
10563	.37	3.1	.01	26	1
10683	.44	2	.02	172	2
10783	.1	3.25	.04	70	1
11083	.07	7.1	.02	16	1
11183	.14	3.73	.01	58	1
11283	1.08	6.38	.01	58	1
11383	.34	2.48	.01	190	2
11483	.28	1.1	.01	84	0
11783	.1	2.65	.02	14	0
11883	.2	.7	.04	50	0
11983	.53	.78	.01	100	2
12083	.81	1.07	.01	136	2
12183	.17	1.03	.01	100	2
12483	.36	2.05	.01	46	0
12783	1.2	1.18	.02	28	0
12883	.6	2.52	.1	106	2
13183	.24	2.6	.1	26	0
20183	.6	1.6	.01	90	2
20283	.39	1.32	.01	42	0
20383	.25	1.26	.04	74	0
20483	.5	1.02	.05	254	2
20783	.18	.63	.08	14	0
20883	.17	1.04	.04	32	0
20983	.38	.3	.04	42	0
21083	.21	.18	.03	54	0
21183	.51	1.15	.03	172	2
21483	.73	.6	.02	96	2
21583	.18	.18	.01	68	0
21683	.09	.18	.01	32	0
21783	.12	.29	.03	74	0
21883	.08	.26	.03	60	0
22183	.08	.22	.04	26	0
22383	.22	.27	.02	88	2
22483	.4	.16	.05	44	0
22583	.46	.64	.04	20	0
22883	1.29	.26	.02	24	0
30283	1.12	.28	.04	18	0
30383	.29	.33	.01	50	0
30483	.15	.25	.01	66	0

Screen Code: 0=Included in analysis; 1=Excluded since Cr>2.9mg/l
2=Excluded since TSS > 87mg/l

Entry of -1 = Data Not Available

Table B-1. Plant F102 Effluent Data (7/21/82-11,21/83)
(Sheet 4 of 6)

DATE	CD(MG/L)	CR(MG/L)	SE(MG/L)	TSS(MG/L)	SCREEN CODE
30783	.12	2.32	.04	42	0
30883	.07	.93	.04	56	0
30983	.23	1.04	.04	50	0
31083	.06	.94	.04	34	0
31183	.17	2.72	.03	86	0
31483	.07	1.61	.02	58	0
31583	.04	1.9	.06	48	0
31683	.18	1.4	.07	64	0
31783	.18	1.2	.04	32	0
31883	.21	.24	.04	0	0
32183	.05	.23	.07	30	0
32283	.13	.15	.04	62	0
32383	.19	.41	.01	20	0
32483	.09	.38	.01	90	2
32583	.1	.31	.01	84	0
32883	.15	.27	.01	42	0
32983	.08	.75	.02	14	0
33083	.09	.49	.04	86	0
33183	.08	.35	.05	26	0
40583	.06	.36	.04	4	0
40683	.05	.46	.02	66	0
40783	.06	.34	.01	24	0
40883	.03	.64	.01	68	0
41183	.03	1.41	.04	28	0
41283	.05	2.8	.03	142	2
41383	.04	1.55	.04	50	0
41483	.04	1.11	.04	62	0
41883	.05	.51	.02	26	0
41983	.06	1.16	.02	62	0
42083	.02	1.06	.1	52	0
42183	.08	.67	.01	118	2
42283	.08	.18	.02	76	0
42583	.05	.22	.02	224	2
42683	.05	.08	.01	80	0
42783	.08	.34	.01	144	2
42883	.07	.02	.03	40	0
42983	.06	.77	.02	68	0
50283	.07	.41	.03	74	0
50383	.08	.63	.05	204	2
50483	.08	.99	.01	122	2
50683	.12	3.92	.01	68	1
51183	.07	3.78	.05	246	2
51283	.09	8.75	.05	288	2
51383	.12	7	.05	372	2
51683	.12	2.02	.04	122	2
51783	.08	1.1	.01	38	0
51883	.12	2.6	.02	42	0
51983	.1	5	.01	120	2
52083	.06	1.45	.03	172	2

Screen Code: 0=Included in analysis; 1=Excluded since Cr>2.9mg/1
2=Excluded since TSS > 87mg/1

Entry of -1 = Data Not Available

Table B-1. Plant F102 Effluent Data (7/21/82-11/21/83)
(Sheet 5 of 6)

DATE	CD(MG/L)	CR(MG/L)	SE(MG/L)	TSS(MG/L)	SCREEN COD
52383	.06	.64	.04	86	0
52483	.09	.85	.02	94	2
52583	.06	.46	.03	150	2
52683	.07	.78	.03	14	0
52783	.09	1.34	.02	198	2
53183	.08	.65	.03	34	0
60183	.66	4.32	.04	248	2
60283	.33	2.9	.02	134	2
60383	.25	1.45	.03	116	2
60683	.22	.54	.05	140	2
60783	.11	.94	.04	98	2
60883	.07	1.36	.03	60	0
60983	.04	.95	.04	132	2
61083	.07	.92	.02	80	0
61383	.09	1.22	.03	50	0
61483	.08	.86	.01	38	0
61583	.1	1.52	.01	142	2
61683	.13	.92	.01	110	2
61783	.09	1.98	.01	122	2
62283	.09	.38	.01	124	2
62383	.05	.25	.01	94	2
62483	.04	.12	.01	80	0
62783	.05	.32	.02	28	0
62883	.09	.12	.03	60	0
62983	.22	.14	.02	154	2
63083	.12	.06	.02	120	2
70183	.05	.08	.01	172	2
71183	.08	2.2	.03	20	0
71283	.09	1.16	.02	32	0
71383	.08	.74	.04	6	0
71483	.44	.82	.04	76	0
71583	.09	1.95	.05	8	0
71883	.51	2.87	.05	54	0
71983	.27	2.68	.03	168	2
72083	.46	.74	.03	50	0
72183	.6	2.6	.04	206	2
81583	.36	1.14	.02	112	2
81683	.51	2.35	.07	130	2
81783	.18	.51	.14	80	0
81883	.1	.1	.38	92	2
81983	.21	.26	.43	534	2
82283	.16	.4	.18	232	2
82483	.19	.42	.31	618	2
82583	.14	.2	.28	578	2
82683	.22	.46	.15	542	2
82983	.12	.29	.07	296	2
83083	.11	.19	.05	172	2
83183	.36	1.69	.03	680	2
90183	.3	1.75	.08	632	2
90283	.25	.89	.04	[illegible]70	2

Screen Code: 0=Included in analysis; 1=Excluded since Cr>2.9mg/l
2=Excluded since TSS> 87mg/l

Entry of -1 = Data Not Available

Table B-1. Plant F102 Effluent Data (7/21/82-11/21/83)
(Sheet 6 of 6)

DATE	CD(MG/L)	CR(MG/L)	SE(MG/L)	TSS(MG/L)	SCREEN CODE
90683	.21	.82	.03	512	2
90783	.27	1.62	.08	756	2
90883	.21	1.7	.06	562	2
90983	.28	1.15	.01	548	2
93083	.42	4.6	.03	502	2
100383	.12	7	.05	274	2
100683	.18	2.43	.02	350	2
100783	.15	1.39	.02	314	2
101083	.22	.86	.03	338	2
101183	.16	1.61	.05	504	2
101283	.1	1.71	.05	444	2
101383	.1	2.38	.06	364	2
101483	.13	3.3	.03	382	2
101983	1.21	1.34	.01	432	2
102083	.75	1.67	.01	304	2
102183	.69	.56	.01	320	2
102483	.28	2.15	.01	268	2
102583	.32	2.2	.01	280	2
102683	.25	3.7	.01	300	2
102783	.18	3.25	.02	328	2
102883	.21	6.1	.02	298	2
103183	.33	2.48	.01	418	2
110183	.28	3.1	.02	330	2
110283	.25	2.65	.02	412	2
110383	.18	1.78	.02	452	2
110483	.2	.77	.01	336	2
110783	.25	.79	.01	196	2
110883	.22	1.57	.01	324	2
110983	.2	1.66	.01	212	2
111083	.17	1.1	.03	332	2
111183	.18	1.55	.03	304	2
111483	.17	1.58	.01	324	2
111583	.21	1.38	.03	436	2
111683	.21	.45	.06	316	2
111783	.13	.18	.3	344	2
111883	.14	.15	-1	352	2
112183	.2	.51	-1	336	2

Screen Code: 0=Included in analysis; 1=Excluded since Cr>2.9mg/l
2=Excluded since TSS> 87mg/l

Entry of -1 = Data Not Available

Table B-2. Plant F102 Effluent Data Screened to Exclude Days When Cr > 2.9mg/l or TSS > 87mg/l

(Sheet 1 of 3)

SCREENED DATA:

DATE	CD (MG/L)	CR (MG/L)	TSS (MG/L)
72182	.1	.6	12
72282	.03	.9	8
72382	.03	1.9	3
72782	.02	2.1	72
80382	.16	2.3	84
80582	.08	1.9	26
80682	.21	.3	56
80982	.11	.2	80
81082	.07	1.5	0
81182	.13	.8	38
81282	.1	.2	26
81382	.06	1.2	80
81682	.1	.9	24
81982	.07	2.1	66
82082	.14	1.5	54
82382	.08	.9	32
82582	.12	.7	72
82782	.05	.4	36
83182	.05	.6	50
90182	.22	.6	58
90282	1.24	.4	40
90382	.57	.1	68
90782	.24	.7	52
90882	.19	2.8	84
91382	.3	1.5	26
91482	.18	2.5	68
91582	.07	1.1	30
92082	.26	2.2	50
92482	.17	1.7	24
92782	.1	2.9	0
93082	.14	2.6	56
100182	.1	1.1	82
100682	.25	.2	66
100882	.33	.2	58
101182	.38	.1	18
101282	.68	.1	62
101882	.72	.52	12
102082	.74	.09	42
102182	1.05	.14	52
102282	.85	.14	26
102582	.44	.5	50
102882	.15	2.5	40
102982	.09	1.74	34
110182	.21	1.45	34
111182	.22	.59	82
112382	.14	.73	30
120182	.08	1.75	70
120682	.07	2.75	10
120782	.08	1.24	78
120982	.06	2.28	74

Table B-2. Plant F102 Effluent Data Screened to Exclude Days When Cr > 2.9mg/l of TSS > 87mg/l

(Sheet 2 of 3)

SCREENED DATA:

DATE	CD(MG/L)	CR(MG/L)	TSS(MG/L)
121382	.1	1.96	72
121582	.19	1.92	48
122082	.1	2	72
10383	.11	2.52	0
11483	.28	1.1	84
11783	.1	2.65	14
11883	.2	.7	50
12483	.36	2.05	46
12783	1.2	1.18	28
13183	.24	2.6	26
20283	.39	1.32	42
20383	.25	1.26	74
20783	.18	.63	14
20883	.17	1.04	32
20983	.38	.3	42
21083	.21	.18	54
21583	.18	.18	68
21683	.09	.18	32
21783	.12	.29	74
21883	.08	.26	60
22183	.08	.22	26
22483	.4	.16	44
22583	.46	.64	20
22883	1.29	.26	24
30283	1.12	.28	18
30383	.29	.33	50
30483	.15	.25	66
30783	.12	2.32	42
30883	.07	.93	56
30983	.23	1.04	50
31083	.06	.94	34
31183	.17	2.72	86
31483	.07	1.61	58
31583	.04	1.9	48
31683	.18	1.4	64
31783	.18	1.2	32
31883	.21	.24	0
32183	.05	.23	30
32283	.13	.15	62
32383	.19	.41	20
32583	.1	.31	84
32883	.15	.27	42
32983	.08	.75	14
33083	.09	.49	86
33183	.08	.35	26
40583	.06	.36	4
40683	.05	.46	66
40783	.06	.34	24
40883	.03	.64	68

Table B-2. Plant F 102 Effluent Data Screened to Exclude Days When Cr> 2.9mg/l or TSS> 87mg/l

(Sheet 3 of 3)

```
SCREENED DATA:
DATE             CD(MG/L)          CR(MG/L)          TSS(MG/L)
 41183             .03              1.41               28
 41383             .04              1.55               50
 41483             .04              1.11               62
 41883             .05              .51                26
 41983             .06              1.16               62
 42083             .02              1.06               52
 42283             .08              .18                76
 42683             .05              .08                80
 42883             .07              .02                40
 42983             .06              .77                68
 50283             .07              .41                74
 51783             .08              1.1                38
 51883             .12              2.6                42
 52383             .06              .64                86
 52683             .07              .78                14
 53183             .08              .65                34
 60883             .07              1.36               60
 61083             .07              .92                80
 61383             .09              1.22               50
 61483             .08              .86                38
 62483             .04              .12                80
 62783             .05              .32                28
 62883             .09              .12                60
 71183             .08              2.2                20
 71283             .09              1.16               32
 71383             .08              .74                6
 71483             .44              .82                76
 71583             .09              1.95               8
 71883             .51              2.87               54
 72083             .46              .74                50
 81783             .18              .51                80
NUMBER OF OBSERVATIONS USED =  130
MEAN =  .204231
STANDARD DEVIATION =  .248913
RANGE:  .02  TO  1.29
```

Table B-3. Plant F102 Paired Influent and Effluent Cadmium Data
(7/21/82 -- 8/5/82)

	WWTP Influent		WWTP Effluent	
Date	**Cadmium, Tot.**	**Cadmium, Dis.**	**Cadmium, Tot.**	**Cadmium, Dis.**
7/21/82	0.65	0.01	0.1	0.01
7/22/82	0.7	0.01	0.03	0.01
7/23/82	1.27	0.01	0.03	0.01
7/26/82	4.19	0.03	0.02	0.01
7/27/82	1.38	0.05	0.02	0.02
7/28/82	1.37	0.03	0.04	0.03
7/29/82	23.10	15.20	0.1	0.04
7/30/82	3.1	0.41	0.08	0.02
8/2/82	11.62	0.35	0.08	0.08
8/3/82	3.22	0.02	0.16	0.02
8/4/82	43.8	0.09	0.04	0.02
8/5/82	8.98	0.05	0.08	0.02

Table B-4. Plant F102 Data Omitted Due to Company Acknowledged Treatment System Upset Conditions

Date	Cd(mg/l)	Cr(mg/l)	Se(mg/l)	TSS(mg/l)
11/3/82	4.6	94.8	0.07	128
11/8/82	0.32	19.25	1.35	72
12/27/82	1.78	5.62	0.02	514
12/28/82	1.65	5.00	0.02	778
1/25/83	11.00	0.55	0.02	46
1/26/83	1.45	2.68	0.02	60
2/22/83	1.25	5.33	0.12	1450
3/1/83	3.28	0.58	0.03	154
4/15/83	0.15	8.60	0.08	626
4/28/83	0.10	3.43	n/a	18
5/5/83	0.15	34.50	0.01	22
5/9/83	0.34	16.25	0.65	1032
5/10/83	0.23	9.75	0.04	700
6/20/83	0.06	41.75	0.03	26
6/21/83	0.72	7.92	0.12	752
7/22/83	3.95	2.62	0.10	n/a
7/25/83	1.35	3.35	0.10	30
7/26/83	7.02	5.02	0.24	220
7/27/83	6.45	3.20	0.16	100
7/28/83	14.80	9.80	0.62	470
7/29/83	6.05	7.85	0.34	246
8/1/83	0.90	5.70	0.11	136
8/2/83	0.66	3.55	0.04	120
8/3/83	1.65	4.98	0.04	146
8/4/83	1.04	5.75	0.06	150
8/5/83	0.64	3.15	0.04	594
8/8/83	4.40	10.90	0.02	188
8/9/83	0.78	26.25	0.31	462
8/10/83	0.44	20.58	0.04	410
8/11/83	1.98	12.38	0.03	50
8/12/83	1.14	10.95	0.04	242
8/23/83	0.47	1.08	0.22	990
9/12/83	6.35	0.47	0.01	440
9/13/83	4.50	96.50	0.02	684
9/14/83	2.30	37.75	0.01	612
9/15/83	1.53	11.00	0.01	646
9/16/83	0.80	0.29	<0.01	90
9/19/83	0.91	5.50	0.01	741
9/20/83	0.88	5.65	0.01	946
9/21/83	0.77	3.78	0.01	858
9/22/83	0.58	1.80	0.01	668
9/23/83	0.38	1.05	0.01	642
9/26/83	0.62	6.83	0.01	1116
9/27/83	0.71	4.60	0.02	862
9/28/83	0.43	3.40	0.03	810
9/29/83	0.35	2.78	0.04	914
10/4/83	0.17	8.00	0.05	456
10/5/83	0.23	4.45	0.03	416
10/17/83	2.82	0.85	0.01	174
10/18/83	3.80	1.32	0.01	376

Table B-5. Plant F128 Effluent Data (1/79-12/83) (sheet 1 of 5)

DATE	EFF FLOW(MGD)	EFF CD(#/DAY)	EFF CD(MG/L)
** 10379	3.56	.89	.0299581
** 11079	3.68	2.76	.0898742
** 11779	3.6	.9	.0299581
** 12479	3.73	.93	.0298777
** 13179	3.46	1.44	.0498724
** 20779	3.8	1.27	.0400492
** 21479	3.43	1.43	.0499592
** 22179	3.34	.56	.0200916
** 22879	3.56	.89	.0299581
** 30779	4.05	1.69	.0500041
** 31479	3.16	3.69	.139931
** 32179	3.22	1.61	.0599161
** 32879	3.39	1.13	.0399441
** 40479	3.65	.91	.029876
** 41179	3.31	1.66	.0600971
** 41879	3.1	4.14	.160034
** 42579	3.07	2.56	.0999253
**50279	3.2	1.87	.070027
**50979	2.97	1.74	.0702048
**51679	3.28	4.38	.16002
**52379	3.36	4.21	.150147
**53079	4.16	2.78	.0800802
**60679	3.34	3.34	.119832
**61379	3.5	2.92	.0999743
**62079	3.09	4.38	.169859
**62779	2.76	2.07	.0898742
**70479	3.11	1.56	.0601088
**71179	3.06	3.83	.149986
**71879	4.2	4.56	.130104
**72579	3.72	4.04	.13014
**80179	3.49	1.17	.040173
**80879	2.14	.54	.030238
**81579	4.01	2.68	.0800874
**82279	3.64	5.77	.189954
**82979	4.49	6	.160132
**90579	4.24	3.18	.0898742
**91279	3.56	3.57	.120169
**91979	3.35	3.35	.119832
**92679	3.21	2.68	.100047
**100379	3.32	3.6	.129939
**101079	3.41	1.62	.0569291
**101779	3.37	5.06	.179926
**102479	3.22	2.69	.100108
**103179	3.47	2.03	.0701036
**110779	3.6	2.64	.087877
**111479	3.76	1.35	.0430249
**112179	3.5	1.17	.0400582
**112879	3.36	1.93	.0688322
**120579	3.42	1.57	.0550107
**121279	3.58	2.36	.0789956
**121979	3.28	1.62	.0591855
**122679	.96	.19	.0237168

**No influent data recorded.

Table B-5. Plant F128 Effluent Data (sheet 2 of 5)

DATE	EFF FLOW(MGD)	EFF CD(#/DAY)	EFF CD(MG/L)
**10280	1.42	.21	.0177217
** 10980	3.42	1.57	.0550107
** 11680	3.62	1.06	.035089
** 12380	3.39	.99	.0349953
** 13080	3.74	1	.0320407
** 20680	3.78	.54	.0171189
** 21380	3.42	1.68	.058865
** 22080	3.51	2.58	.0880818
** 22780	3.8	3.81	.120148
** 30580	3.42	2.37	.0830417
** 31280	3.16	1.48	.056124
** 31980	3.7	1.54	.0498761
** 32680	3.54	1.89	.0639782
** 40280	3.26	1.44	.0529321
** 40980	3.36	1.49	.0531399
** 41680	3.7	.96	.0310916
** 42380	3.48	1.02	.0351232
** 43080	3.23	1.19	.0441487
**50780	3.43	3.72	.129964
**51480	3.27	14.74	.540161
**52180	3.06	2.55	.0998602
**52880	2.95	2.34	.0950534
**60480	2.81	5.16	.220048
**61180	2.97	6.2	.250155
**61880	3.27	2.62	.0960124
**62580	3.16	2.11	.0800146
**70280	2.53	.91	.0431017
**70980	2.54	.81	.0382142
**71680	3.35	1.2	.042925
**72380	3	1.73	.0691033
**73080	3.08	1.21	.047077
**82080	2.33	.1	5.14302E-03
**82780	2.71	.11	4.86404E-03
**90380	2.83	.12	5.08123E-03
**91080	3.52	.88	.0299581
**91780	2.94	.25	.0101898
**92480	2.7	.68	.03018
**100180	2.65	.44	.0198967
**100880	2.94	1.96	.0798882
**101580	2.9	1.21	.049999
102280	2.96	.74	.0299581
**102980	2.2	.55	.0299581
**110580	2.79	1.4	.0601309
**111280	2.79	.7	.0300654
**111980	2.45	1.23	.0601607
*112680	3	2	.0798882
120380	2.82	.71	.0301705
**121080	3.16	1.32	.0500565
121780	3.37	1.97	.0700503

*Data included in the screened data set since influent Cd≥1.2 mg/l.

**No influent data recorded.

Table B- 5. Plant F128 Effluent Data (sheet 3 of 5)

DATE	EFF FLOW(MGD)	EFF CD(#/DAY)	EFF CD(MG/L)
*10781	2.29	1.34	.0701202
11481	2.41	1.41	.0701093
*12181	2.49	1.04	.0500504
**12881	3.12	1.56	.0599161
**20481	2.88	.72	.0299581
*21181	2.95	3.2	.129988
***21881	3.12	2.86	.109846
22581	3.09	2.06	.0798882
*30481	3.05	1.71	.0671846
31181	3.32	1.11	.0400644
31881	3.27	1.36	.0498385
32581	3.49	1.46	.0501304
40181	3.45	1.44	.0500169
40881	3.39	1.13	.0399441
*41581	3.69	1.23	.0399441
42281	3.74	1.87	.0599161
42981	3.62	.91	.0301236
50681	3.6	1.2	.0399441
*51381	3.63	3.33	.109929
*52081	4.16	2.43	.0699982
52781	3.89	.97	.0298811
*60381	3.58	5.68	.190125
*61081	3.93	5.25	.160081
*61781	3.72	1.55	.0499301
62481	3.98	1.99	.0599161
*70181	4.16	3.12	.0898742
***72281	2.26	1.51	.0800649
***72981	3.2	.8	.0299581
80581	3.2	.8	.0299581
*81281	3.99	1.66	.049855
81981	2.44	2.24	.11001
*82681	3.81	1.27	.0399441
*90281	4.45	4.46	.120102
*90981	3.86	.81	.0251462
*91681	3.55	1.9	.0641356
92381	4.01	3.68	.109971
93081	3.47	1.82	.0628515
100781	3.57	1.67	.056056
101481	3.61	1.36	.0451446
102181	3.93	.79	.0240884
*102881	4.38	4.02	.109983
110481	3.71	.71	.0229329
111181	3.67	.61	.0199176
111881	3.57	.89	.0298741
***112581	3.06	1.07	.0419021
120281	3.07	1.51	.0589403
*120981	2.57	1.27	.0592167
121681	2.88	3.61	.150206
122381	2.36	1.58	.0802267

*Data included in the screened data set since influent Cd$\geq$1.2 mg/l.

**No influent data recorded

***Flow discrepancy between influent and effluent records.

Table B-5. Plant F128 Effluent Data (sheet 4 of 5)

DATE	EFF FLOW(MGD)	EFF CD(#/DAY)	EFF CD(MG/L)
10682	2.49	.77	.0370566
11382	2.46	.62	.0302016
12082	2.74	.87	.0380489
*12782	2.55	9.28	.436095
20382	2.69	1.41	.0628117
*21082	2.8	.98	.0419413
21782	2.4	.28	.0139804
22482	2.39	.5	.0250695
*30382	2.79	1.65	.0708685
31082	2.59	.35	.0161935
31782	2.98	.72	.0289528
32482	2.87	.43	.017954
33182	2.1	1.54	.087877
*40782	2.46	1.03	.0501737
*41482	2.83	.78	.033028
*42182	2.69	2.69	.119832
42882	2.96	1.48	.0599161
***50582	2.67	2.23	.100085
51282	2.76	1.15	.0499301
51982	2.9	.97	.0400818
52682	3.13	.52	.0199082
60282	2.9	.48	.0198343
*60982	3.17	2.12	.0801402
*61682	3.06	9.96	.390042
62382	3.07	1.02	.039814
*63082	3.05	3.31	.130047
***70782	.77	.19	.029569
72182	2.54	.85	.0401013
72882	3.2	.88	.0329539
80482	3.12	.65	.024965
81182	3.36	1.12	.0399441
81882	2.75	.8	.0348603
82582	4.46	1.12	.0300924
*90182	2.97	5.95	.240068
90882	2.4	.7	.0349511
91582	.96	.32	.0399441
92282	2.31	.58	.0300878
92982	2.63	.55	.02506
100682	2	.25	.014979
101382	1.8	.23	.0153119
***102082	2.58	.54	.0250812
102682	2.91	.36	.0148246
110382	3.25	.57	.0210167
111082	3	.38	.0151788
111782	2.91	.61	.0251195
120182	1.67	.29	.0208092
120882	2.5	.63	.0301977
121582	3.09	.52	.0201659
122282	2.83	.71	.0300639

*Data included in the screened data set since influent Cd≥1.2 mg/l.
***Flow discrepancy between influent and effluent records.

Table B-5. Plant F128 Effluent Data (sheet 5 of 5)

DATE	EFF FLOW(MGD)	EFF CD(#/DAY)	EFF CD(MG/L)
10583	2.4	.38	.0189734
11283	3.05	1.37	.0538263
*11983	2.72	.91	.0400909
12683	2.92	2.17	.0890534
20283	2.3	.88	.0458489
20983	3.03	1.09	.043108
*21683	2.95	3.94	.160047
*22383	2.58	1.57	.0729212
30283	2.13	.82	.0461326
*30983	2.73	1.39	.0610135
32383	2.17	1.01	.0557745
33083	2.59	.58	.026835
40683	2.12	.69	.039002
41383	2.67	.67	.0300703
*42083	2.58	5.6	.260101
42783	1.84	.57	.037122
*50483	2.83	5.9	.249827
51183	2.02	.32	.0189833
*51883	2.55	16.39	.770216
52583	2.11	1.94	.110178
60183	1.78	.43	.0289482
60883	2.8	.72	.030814
61583	2.18	.2	.0109938
62283	2.24	.24	.0128392
62983	2.19	.75	.0410384
70683	.93	.61	.0785997
71383	1.26	.14	.0133147
72083	2.46	.31	.0151008
72783	2.77	1.46	.0631607
80383	2.95	4.68	.190107
81083	2.92	.83	.0340619
81783	2.86	1.29	.0540502
82483	2.78	1.18	.050864
*83183	2.51	1.4	.0668387
90783	2.36	.69	.0350357
91483	2.74	1.6	.069975
92183	2.78	2.16	.0931071
92883	2.48	1.06	.0512186
100583	3.55	.65	.0219411
101283	2.97	.37	.0149206
101983	3.37	.7	.024891
102683	3.13	.57	.0218225
110283	2.66	1.04	.0468517
110983	3.53	1.59	.0539754
*111683	3.16	5.8	.219945
*113083	3.27	7.37	.270081
120783	3.67	2.42	.0790175
**120883	3.12	-1	X-XXXXXXXX ****
120983	2.9	-1	X-XXXXXXXX ****
121483	3.42	1.43	.0501053
**122083	2.87	1.82	.0759912
122183	3.09	1.57	.0608856

*Data included in the screened data set since influent Cd≥1.2 mg/l.

**No influent data recorded.

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****Negative 1 entry indicates Not Available.